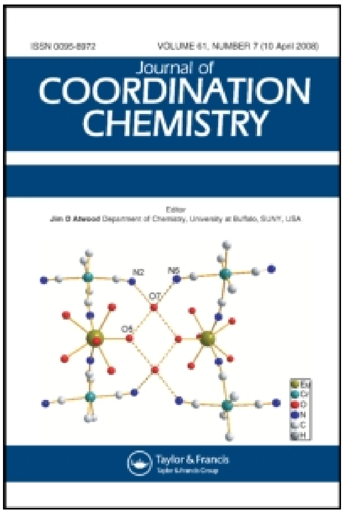


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, characterization and crystal structures of Ni(II), Cd(II) complexes with <i>N</i>-(2-propionic acid)-salicyloyl hydrazone and bipy/phen

Wang-Ting Wu[a,b]; Shui-Yang He[b]; Feng Liu[b]; Feng-Ying Chen[b]; Yao-Yu Wang[b]; Qi-Zhen Shi[b]
[a] Capital Museum, Beijing 100045, China [b] Department of Chemistry, Northwest University and Shaanxi Key Laboratory of Physico-Inorganic Chemistry, Shaanxi 710069, China

To cite this Article Wu, Wang-Ting , He, Shui-Yang , Liu, Feng , Chen, Feng-Ying , Wang, Yao-Yu and Shi, Qi-Zhen(2008) 'Synthesis, characterization and crystal structures of Ni(II), Cd(II) complexes with **<i>N</i>**-(2-propionic acid)-salicyloyl hydrazone and bipy/phen', Journal of Coordination Chemistry, 61: 17, 2703 — 2714

To link to this Article: DOI: 10.1080/00958970801958519

URL: http://dx.doi.org/10.1080/00958970801958519

Journal of Coordination Chemistry
Vol. 61, No. 17, 10 September 2008, 2703–2714

Synthesis, characterization and crystal structures of Ni(II), Cd(II) complexes with *N*-(2-propionic acid)-salicyloyl hydrazone and bipy/phen

WANG-TING WU†‡, SHUI-YANG HE*‡, FENG LIU‡, FENG-YING CHEN‡,
YAO-YU WANG‡ and QI-ZHEN SHI‡

†Capital Museum, Beijing 100045, China
‡Department of Chemistry, Northwest University and Shaanxi Key Laboratory of Physico-Inorganic Chemistry, Xi'an, Shaanxi 710069, China

(*Received 18 June 2007; in final form 20 November 2007*)

The ligand *N*-(2-propionic acid)-salicyloyl hydrazone(H_3L, **1**) and its new transition metal(II) complexes [NiHL(bipy)H_2O] (**2**), [CdHL(bipy)$(H_2O)_2]_2 \cdot 2H_2O$ (**3**) and [NiHL(phen)$H_2O] \cdot H_2O$ (**4**) (HL is a dianion, bipy = 2,2′-bipyridine and phen = 1,10-phenanthroline) were synthesized and characterized on the basis of elemental analyses, IR, ^{1}H NMR, molar conductivity and thermal analysis. Single crystal X-ray diffraction showed that **1** is in keto form and connected by hydrogen bonds to form a two-dimensional supermolecular compound. Complexes **2** and **4** have the same structure with distorted meridional octahedral geometry with **1** as a tridentate ligand with keto-form coordination by azomethine, carboxyl O and acyl O. In **3**, ligand **1** bridges two Cd(II) atoms by μ_2-O of carboxyl. H-bonding is an important weak interaction for constructing supermolecular frameworks. There are π–π interactions between bipy or phen rings in **3** or **4**, respectively.

Keywords: *N*-(2-propionic acid)-salicyloyl hydrazone; Transition metal complexes; Bipy; Phen; Crystal structure; H-bonding; π–π interaction

1. Introduction

The concept of building units is very helpful in elucidating and understanding the structural characteristics of assemblies in crystal engineering, and connection by metal-ligand interactions and intermolecular interactions such as hydrogen bonds and π–π stacking are the two main strategies [1, 2].

Hydrazone has interesting coordination behavior and diverse applications [3, 4]. Acyl hydrazone ligands bearing both nitrogen and oxygen donors which exhibit both hard and soft base character could form more stable complexes than polyoxa or polyaza ligands [5]. Aroyl hydrazones have been the subject of investigation due to their versatile chelating behavior, coordinating in the keto form, dehydrogenation conjugation and enol form [6–10]. The valence of acyl hydrazone is multiple [11–15]; *N*-(2-propionic acid)-salicyloyl hydrazone has potential H-bonding sites.

---

*Corresponding author. Email: xdchemistry411@126.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970801958519

Many of physiologically-active aroylhydrazone complexes find application in the treatment of diseases such as tuberculosis, tumor, cancer and insecticides [16–21]. Chelation therapy is the most successful means of treatment of heavy metal poisoning [22–25]. 2,2′-bipyridine and 1,10-phenanthroline have aromatic π clouds, are good rigid ligands, and exhibit numerous beneficial biological activities [26, 27].

Here we report the synthesis and characterization by single crystal X-ray diffraction, elemental analysis and spectroscopic measurements of the hydrazone H_3L, two Ni(II) complexes and one heavy metal Cd(II) complex, and discuss the metal-ligand interactions and intermolecular interactions such as hydrogen bonds and π–π stacking.

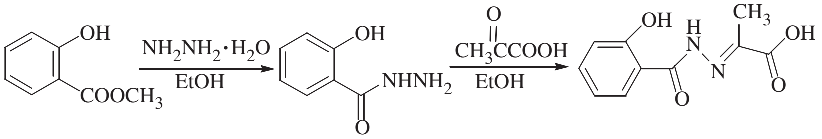
2. Experimental

2.1. *Reagents and materials*

All chemicals and solvents were of analytical grade. IR spectra were recorded with an EQUINOX55 spectrophotometer using KBr pellets. Elemental analyses of C, H, and N were performed by a Perkin-Elmer model 2400 elemental analyzer. Molar conductance measurements were made using a DDS-11A conductivity meter. ^{1}H NMR spectra were recorded on an INOVA-400 NMR spectrometer using $(CD_3)_2SO$ as the solvent. TG-DTG curves are obtained with a NETZSCH STA 499C thermal analyzer with a heating rate of 10°C min^{-1}. The X-ray diffraction data for the crystals were collected on a Bruker Smart-1000 CCD X-ray single crystal diffractometer.

2.2. *Preparation of the ligand*

Salicyloyl hydrazine was prepared according to the reported method [28].



84 mL pyruvic acid was added to solution of the salicyloyl hydrazide (6.09 g) in anhydrous alcohol (30 mL). The mixture was stirred on a water bath (80°C) for 2 h, the precipitate filtered, recrystallized from alcohol and washed by ether. The melting point is 216–217°C. We have reported the synthesis of **1** [14], but the crystal structure has never been reported. **1** was dissolved in the mixed solvent of methanol and water (v/v = 2 : 1) and stirred 5 h, then filtrated. After two weeks at room temperature, the colorless claval crystal $[(C_{10}H_{10}O_4N_2) \cdot 2H_2O]$ (**1**) suitable for X-ray measurement was obtained.

2.3. *Preparation of complexes*

$M(NO_3)_2 \cdot nH_2O$ (M=Ni, Cd) (0.02 mmol), H_2L (0.02 mmol) and bipy/phen (0.02 mmol) were dissolved in 50 mL mixed aqua-ethanol, respectively, and then mixed. A spot of triethylamine was added to the above suspension. After stirring at

80°C for 1 h, the precipitate was separated by filtration, washed several times with water, hot ethanol, and dried in a vacuum. The resulting solution was allowed to evaporate slowly at room temperature for several days to obtain suitable crystals for X-ray diffraction measurement. The procedure of $[NiHL(phen)H_2O] \cdot H_2O$ was similar to that for $[NiHL(bipy)H_2O]$, except that phen was used instead of bipy.

$$M(NO_{3)2} \cdot nH_2O + H_2L + \text{bipy/phen} \xrightarrow[H_2O+C_2H_5OH]{\text{triethylamine}} \text{complexes}$$

2.4. *X-ray diffraction data collection and reduction*

Single crystal X-ray diffraction measurements of both compounds were carried out with a Bruker Smart 1000 CCD X-ray diffractometer. Intensities of reflections were measured at 298 K using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) with ω scan mode. Empirical absorption correction was applied using SABADS. Crystal structures of **1**, **2**, **3** and **4** were solved by direct methods and Fourier-difference syntheses. All non-hydrogen atoms were refined anisotropically. Full matrix least-squares refinement on F^2 was performed by the SHELXL-97 program package. The final R_1, wR_2 and other refinement parameters are presented in table 1.

3. Results and discussion

3.1. *Characterization and spectroscopic studies*

All complexes are freely soluble in DMF and DMSO, sparingly soluble in water, ethanol and methanol, but insoluble in benzene, acetone and diethyl ether. The molar conductivity of the complexes is $3 \sim 7\,\Omega^{-1}\,cm^2\,mol^{-1}$ in DMF (table 2) showing non-electrolytes in DMF [29]. The elemental analyses of the complexes are consistent with the composition.

The main IR stretching frequencies of the ligand and complexes are tabulated in table 3 in the region 4000–400 cm^{-1}. The absorption band around 1756 cm^{-1}, assignable to $\nu_{C=O}$ (COOH) of free H_3L, has been replaced by two new bands, $\nu_{s,COO}$ and $\nu_{as,COO}$, and the $\Delta\nu(\nu_{as} - \nu_s)$ are 254, 80, and 267 cm^{-1}, respectively, in the three complexes. The shifts suggest that the carboxyl group is monodentate coordinating to the Ni(II) (for **2** and **4** complexes) and bidentate μ_2 bridge ligand for Cd(II) [30]. The 1616 cm^{-1} ($\nu_{C=O}$) vibration of the free ligand is red-shifted in the complexes, showing the oxygen (C=O) bound to metal. The 1532 cm^{-1} (δ_{NHN}) vibration of the free ligand disappears in **2** and **4** and becomes weak in **3** indicating the hydrogen of –NHN= is lost in **2** and **4** and partly lost in **3**. The $\nu_{C=N}$ at 1588 cm^{-1} in the ligand has red-shifted in all complexes, confirming that the azomethine nitrogen coordinates to M(II) [31]. The complexes show a wide band between 3600 and 3500 cm^{-1}, attributable to the –OH group involved in intermolecular hydrogen bonding [32]. The in-plane and out-of-plane vibrations of water observed near 750 and 570 cm^{-1} are associated with coordinated water [33]. The 1454 cm^{-1} ($\nu_{C=N}$) vibration of free bipy is red-shifted in the complexes, showing nitrogen bound to metal [27]. This IR spectroscopic analysis is in agreement with the X-ray diffraction crystal structure of the complexes.

Table 1. Crystal and structure refinement summary for **1**, **2**, **3** and **4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{10}H_{14}N_2O_6$	$C_{20}H_{18}N_4O_5Ni$	$C_{20}H_{20}CdN_4O_6$	$C_{22}H_{20}N_4O_6Ni$
Formula weight	258.23	453.09	525.81	495.11
Crystal system, space group	Orthorhombic, *F*dd2	Monoclinic, *P*21/*c*	Triclinic, $P\bar{1}$	Monoclinic, *P*21/*n*
Unit cell dimensions (Å,°)				
a	28.887(9)	7.4418(12)	11.9891(6)	7.104(3)
b	32.733(10)	28.821(5)	12.3488(7)	25.419(10)
c	4.9281(14)	9.4404(15)	14.4588(8)	11.769(5)
α	90	90	86.6680(10)	90
β	90	109.729(2)	82.8070(10)	98.062(7)
γ	90	90	74.1190(10)	90
Volume (Å^3)	4660(2)	1905.9(5)	2042.09(19)	2104.2(14)
Z, calculated density (Mg m^{-3})	8, 1.592	4, 1.579	4, 1.710	4, 1.560
Absorption coefficient (mm^{-1})	0.127	1.06	1.116	0.971
θ range for data collected (°)	1.88–25.09	1.41–25.10	2.20–26.93	1.92–25.10
$F(000)$	2304	936	1060	1020
Limiting indices	$-34 \leq h \leq 33$	$-8 \leq h \leq 8$	$-14 \leq h \leq 14$	$-8 \leq h \leq 8$
	$-36 \leq k \leq 38$	$-34 \leq k \leq 15$	$-11 \leq k \leq 14$	$-9 \leq l \leq 14$
	$-5 \leq l \leq 5$	$-11 \leq l \leq 11$	$-14 \leq l \leq 17$	$-29 \leq k \leq 30$
Reflections collected/unique	5890/1957	9538/3393	10370	10756/3749
Completeness to $\theta = 25.10$ (%)	100.00	100.00	98.40	99.80
Max. and min. transmission	0.283 and −0.231	0.9014 and 0.8080	0.8704 and 0.7336	0.9431 and 0.7997
Goodness-of-fit on F^2	1.113	1.021	1.027	1.034
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0439$	$R_1 = 0.0527$	$R_1 = 0.0271$	$R_1 = 0.0490$
	$wR_2 = 0.1317$	$wR_2 = 0.1037$	$wR_2 = 0.0624$	$wR_2 = 0.1104$
R indices (all data)	$R_1 = 0.0505$	$R_1 = 0.1005$	$R_1 = 0.0505$	$R_1 = 0.0890$
	$wR_2 = 0.1345$	$wR_2 = 0.1246$	$wR_2 = 0.0662$	$wR_2 = 0.1276$
Largest diff. peak/hole (e Å^{-3})	0.283 and −0.231	0.370 and −0.408	0.393 and −0.579	0.787 and −0.339

^1H NMR spectra of **1** and **3** were obtained at room temperature in $(CD_3)_2SO$ solution. The proton labels of the ligand are shown in scheme 1 and the data in table 4. The proton chemical shifts of H_aL disappear in **3**. All proton signals in the complex are shifted to low field with respect to the free ligand. The area ratios in **3** are $b:c:d:e:f:g:h:I:j = 3.02:0.53:0.46:4.10:2.05:2.00:2.06:2.08:4.21$, respectively;

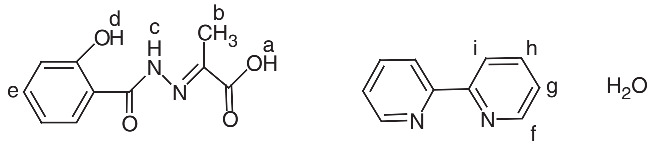
Table 2. Elemental analysis and molar conductivity.

			C (%)		H (%)		N (%)		M (%)		
Sample	Color	Yield	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Λ(U)[a]
1	Colorless	85	54.05	54.23	4.54	4.50	12.61	12.59			
2	Laurel-green	62	53.02	53.00	4.00	4.20	12.37	12.37	12.95	12.86	3.32
3	Yellow	70	51.26	51.00	4.30	4.38	11.96	12.02	11.99	12.39	4.38
4	Laurel-green	71	53.37	53.40	4.07	4.01	11.32	11.38	11.85	11.80	6.72

[a] $U = \Omega^{-1}\,cm^2\,mol^{-1}$.

Table 3. Some IR data of the ligand and complexes (cm^{-1}).

Sample	ν_{OH}	ν_{NH}	$\nu_{C=O}$	$\nu_{C=N}$	ν_{COO^-} as	ν_{COO^-} s	$\Delta\nu$ ($\nu_{as} - \nu_s$)	δ_{HOH}	$\nu_{C=N}$ (bipy/phen)
1		3400	1616	1588					
2	3353		1602	1571	1589	1335	254	758, 573	1446
3	3369	3432(w)	1608	1569	1540	1460	80	743, 564	1435
4	3357		1602	1571	1611	1344	267	761, 584	1440



Scheme 1. Labels of the hydrogen.

Table 4. ^1H NMR data of the ligands and complex **3**.

		H_3L	Bipy	$[CdHL(bipy)(H_2O)_2]_2 \cdot 2H_2O$
H_3L	δ_a	13.83	—	—
	δ_b	2.13	—	2.20(3H)
	δ_c	11.78	—	11.98(0.5H)
	δ_d	11.38	—	11.42(0.5H)
	δ_e	6.93–7.98	—	6.95–8.11(4H)
Bipy	δ_f	—	8.71	8.92(2H)
	δ_g	—	7.47	8.24(2H)
	δ_h	—	7.96	8.50(2H)
	δ_i	—	8.42	8.66(2H)
$\delta(H_2O)$		—	—	3.33, 3.45

protons c and d are half-lost in the complex, which is consistent with the crystal structure and IR. The proton signals of H_2O at 3.33 and 3.45 ppm show that H_2O molecules exist in the complex. The chemical shifts of the protons on the 2,2′-bipyridine indicate coordination to metal.

3.2. *Description of the crystal structure*

Selected bond lengths and bond angles of the crystals are listed in tables 5, 6, 7 and 8 for ligand, [NiHL(bipy)H_2O], [CdHL(bipy)$(H_2O)_2$]$_2 \cdot 2H_2O$ and [NiHL(phen)H_2O]$\cdot H_2O$, respectively. The molecular structures are shown in figure 1 ((**1**) ligand, (**2**) [NiHL(bipy)H_2O], (**3**) [CdHL(bipy)$(H_2O)_2$]$_2 \cdot 2H_2O$, and (**4**) [NiHL(phen)H_2O]$\cdot H_2O$), and the crystal packing diagrams are depicted in figure 2.

Table 5. Selected bond lengths (Å) and angles (°) of **1**.

N(1)–C(7)	1.366(3)	O(1)–C(5)	1.352(4)	O(3)–C(9)	1.203(4)
N(1)–N(2)	1.364(3)	O(2)–C(7)	1.230(3)	O(4)–C(9)	1.322(4)
N(2)–C(8)	1.281(4)				
C(7)–N(1)–N(2)	120.0(2)	C(2)–C(1)–C(6)	122.2(3)	C(4)–C(3)–C(2)	120.2(3)
C(8)–N(2)–N(1)	116.8(2)	C(1)–C(2)–C(3)	120.0(3)	C(3)–C(4)–C(5)	120.9(3)
O(1)–C(5)–C(4)	121.1(2)	O(1)–C(5)–C(6)	119.3(3)	O(2)–C(7)–N(1)	121.1(3)
O(2)–C(7)–C(6)	122.1(3)	N(1)–C(7)–C(6)	116.8(2)	N(2)–C(8)–C(10)	127.0(3)
N(2)–C(8)–C(9)	114.7(3)	O(3)–C(9)–O(4)	123.4(3)	O(3)–C(9)–C(8)	122.1(3)
O(4)–C(9)–C(8)	114.5(3)				

Table 6. Selected bond lengths (Å) and angles (°) of **2**.

Ni(1)–N(3)	1.979(4)	Ni(1)–O(4)	2.095(4)	O(1)–C(17)	1.261(5)
Ni(1)–N(2)	2.069(4)	Ni(1)–O(2)	2.100(3)	O(5)–C(15)	1.360(5)
Ni(1)–N(1)	2.077(4)	Ni(1)–O(1)	2.127(3)	N(4)–C(17)	1.357(5)
N(3)–N(4)	1.380(5)				
N(3)–Ni(1)–N(2)	168.63(15)	N(2)–Ni(1)–O(4)	94.67(16)	N(1)–Ni(1)–O(2)	97.98(13)
N(3)–Ni(1)–N(1)	97.18(15)	N(1)–Ni(1)–O(4)	166.54(14)	O(4)–Ni(1)–O(2)	93.81(13)
N(2)–Ni(1)–N(1)	78.44(16)	N(3)–Ni(1)–O(2)	77.81(14)	N(3)–Ni(1)–O(1)	76.90(13)
N(3)–Ni(1)–O(4)	91.63(14)	N(2)–Ni(1)–O(2)	92.31(13)	O(4)–Ni(1)–O(1)	84.57(13)
N(2)–Ni(1)–O(1)	113.09(13)	N(1)–Ni(1)–O(1)	87.53(13)	O(2)–Ni(1)–O(1)	154.60(12)

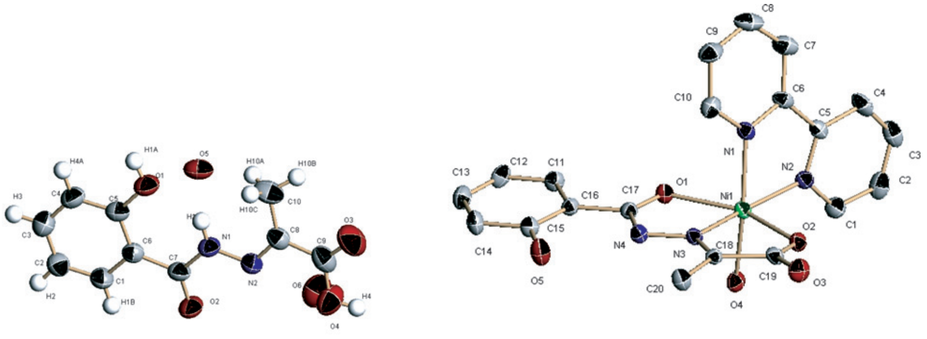
Table 7. Selected bond lengths (Å) and angles (°) of **3**.

Cd(1)–O(3)	2.296(2)	Cd(1)–N(2)	2.305(2)	Cd(1)–N(4)	2.344(3)
Cd(1)–N(3)	2.366(3)	Cd(1)–O(9)	2.4247(19)	Cd(1)–O(2)	2.460(2)
Cd(1)–O(4)	2.462(2)	O(1)–C(5)	1.345(4)	O(6)–C(21)	1.320(4)
O(2)–C(7)	1.256(3)	O(7)–C(27)	1.247(3)	N(1)–C(7)	1.340(4)
N(6)–C(27)	1.350(4)				
O(3)–Cd(1)–N(2)	89.24(9)	O(3)–Cd(1)–N(4)	158.62(9)	N(2)–Cd(1)–N(4)	105.09(9)
O(3)–Cd(1)–N(3)	91.27(10)	N(2)–Cd(1)–N(3)	157.52(9)	N(4)–Cd(1)–N(3)	69.40(10)
O(3)–Cd(1)–O(9)	81.56(8)	N(2)–Cd(1)–O(9)	120.52(8)	N(4)–Cd(1)–O(9)	103.69(8)
N(3)–Cd(1)–O(9)	81.74(8)	O(3)–Cd(1)–O(2)	80.09(8)	N(2)–Cd(1)–O(2)	66.62(8)
N(4)–Cd(1)–O(2)	90.97(8)	N(3)–Cd(1)–O(2)	91.34(8)	O(9)–Cd(1)–O(2)	160.23(7)
O(3)–Cd(1)–O(4)	119.15(8)	N(2)–Cd(1)–O(4)	67.18(7)	N(4)–Cd(1)–O(4)	81.51(8)
N(3)–Cd(1)–O(4)	130.65(8)	O(9)–Cd(1)–O(4)	67.17(7)	O(2)–Cd(1)–O(4)	129.16(7)

For *N*-(2-propionic acid)-salicyloyl hydrazone(H_3L), the bond length of acyl C=O (1.230 Å), shows it to be keto form. The structure of **1** reveals quasi coplanarity of the whole molecular skeleton, and shows the expected *trans*-C=N–N–C conformation. The molecules form a two-dimensional reticulation along a (see figure 2a). The intramolecular hydrogen bond between the phenolic O1 and the azomethine N1 forms a six-numbered ring sharing the same edge with phenol ring

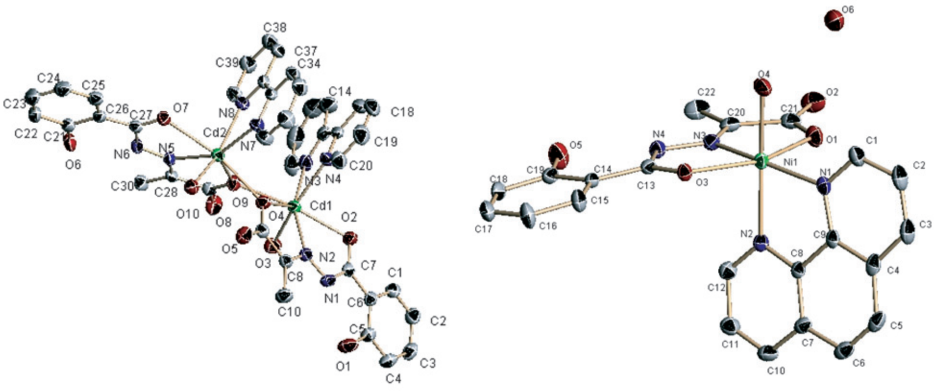
Table 8. Selected bond lengths (Å) and angles (°) of **4**.

Ni(1)–N(3)	1.979(3)	Ni(1)–N(2)	2.086(3)	O(3)–C(13)	1.272(4)
Ni(1)–O(4)	2.060(4)	Ni(1)–O(3)	2.114(3)	O(5)–C(19)	1.347(6)
Ni(1)–N(1)	2.080(3)	Ni(1)–O(1)	2.118(3)	N(4)–C(13)	1.347(5)
N(3)–N(4)	1.371(4)				
N(3)–Ni(1)–O(4)	96.72(14)	N(1)–Ni(1)–N(2)	79.27(13)	N(3)–Ni(1)–O(1)	77.59(13)
N(3)–Ni(1)–N(1)	168.45(13)	N(3)–Ni(1)–O(3)	76.79(12)	O(4)–Ni(1)–O(1)	92.32(14)
O(4)–Ni(1)–N(1)	89.96(14)	O(4)–Ni(1)–O(3)	87.57(12)	N(1)–Ni(1)–O(1)	92.78(13)
N(3)–Ni(1)–N(2)	95.83(13)	N(1)–Ni(1)–O(3)	113.03(11)	N(2)–Ni(1)–O(1)	99.29(13)
O(4)–Ni(1)–N(2)	164.47(15)	N(2)–Ni(1)–O(3)	86.41(12)	O(3)–Ni(1)–O(1)	154.19(12)



1 (ligand)

2 ([NiHL(bipy)H_2O])



3 ($[CdHL(bipy)(H_2O)_2]_2\cdot 2H_2O$)

4 ($[NiHL(phen)H_2O]\cdot H_2O$)

Figure 1. Structures of all the complexes.

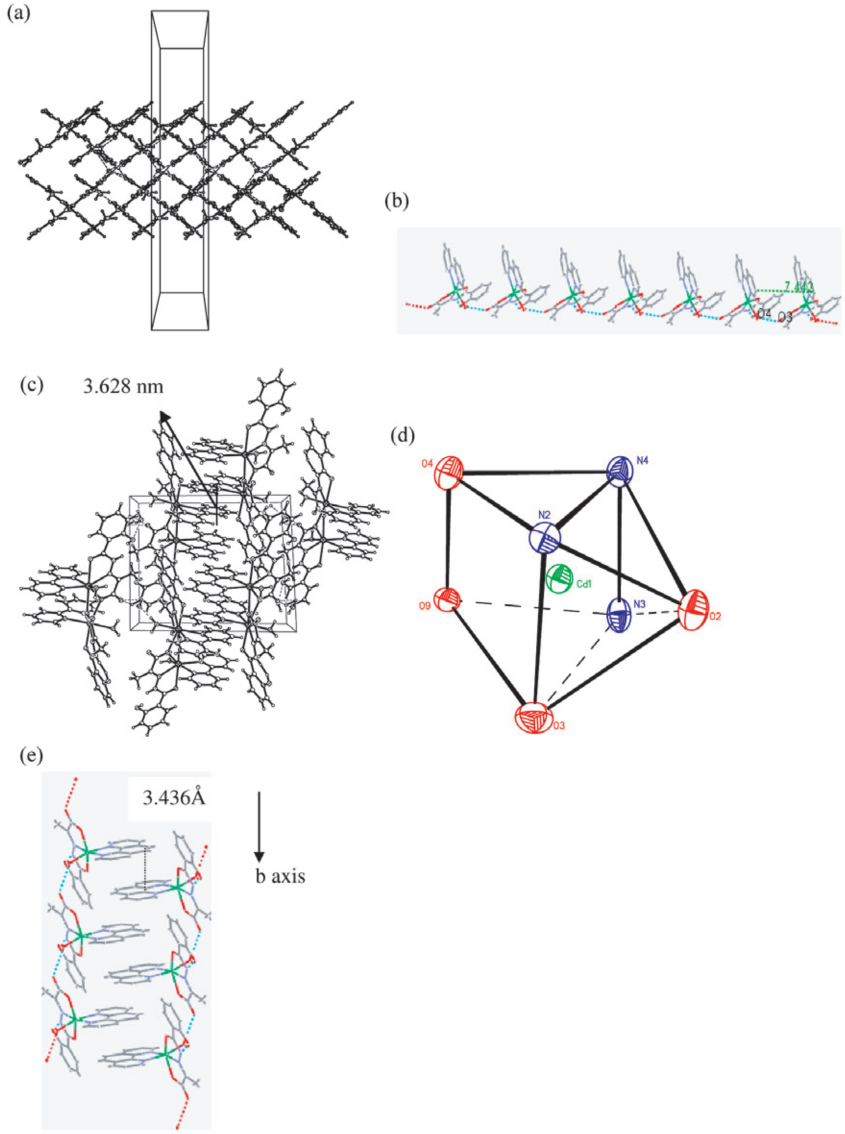


Figure 2. (a) Packing diagram for **1**. (b) Complex **2** forms infinite one-dimensional chain by the hydrogen bond along *b* axis. (c) Packing diagram for **3**. (d) The polyhedron for **3**. (e) The intermolecular π–π stacking for **4**.

(O1 $\cdots$ H–N1 = 2.609 Å, $\angle$NHO = 136.12°). Adjacent molecules are hydrogen bonded through water of crystallization. The intermolecular hydrogen bonds (O4 $\cdots$ H–O5 = 2.931 Å, N2 $\cdots$ H–O5 = 2.997 Å, O2 $\cdots$ H–O5 = 2.736 Å) determine a molecular conformation corresponding to ONO chelating behavior.

Figure 1.2 shows the neutral nickel complex [NiHL(bipy)H_2O] where *N*-(2-propionic acid)-salicyloyl hydrazone is ONO tridentate, bipy a bidentate. HL and bipy are almost mutually perpendicular (dihedral angle between chelation systems = 97.4°), with the bipyridine nitrogen (N1) and oxygen (O4) *trans* to each other (N1–Ni–O4 = 166.54(14)°), thus generating a distorted octahedral coordination for Ni(II). Due to the MA_3B_3 framework complex (where M is metal, A and B are different coordinated atoms), it can adopt two conformations (facial (fac-) and meridional (mer-)). In this instance, the complex [NiL(bipy)H_2O] adopts the meridional orientation in the solid state. The deviation from ideal geometry is due to strains induced by the tridentate (O, N, O) and coordinated water molecule (N2–Ni–N3 = 168.63(15)°, O2–Ni–O1 = 154.60(12)°), which cause a tetrahedral distortion of the O1,O2,N2,N3 equatorial plane of the coordination octahedron. Due to chelation strains, the bond distances involving azomethine nitrogens (2.069–2.077 Å) are longer than those of pyridinic donors (1.979 Å) [33]. Comparing the distances to C–O (1.43 Å) and C=O (1.22 Å), the bond lengths of O(1)–C(17) is 1.261(5) Å, indicating keto form [9]. The tridentate ligand can form two five-numbered rings shared the same edge, two chelated rings are coplanar, indicating its coordination is strong. By comparison of the ligand in nickel complex and the free ligand, the planarity of the whole molecule is reduced (dihedral angle between phenyl and the rest of ligand increases from 3.3 to 12.0°) caused by chelation and hydrogen bond strains after coordination. There is a significant twist (9.4°) between the two halves of the bipyridine [26]. There are intramolecular and intermolecular hydrogen bond interactions; the intramolecular interaction is between the phenolic hydroxy oxygen (O5) and imine nitrogen (N4) (O5–H $\cdots$ N4 = 2.527 Å with bond angle 146.77°), while the intermolecular interaction is between the water and two carboxylic oxygens of two neighboring molecules at distances O4–H $\cdots$ O2 = 2.787 Å and O4–H $\cdots$ O3 = 2.786 Å, and bond angles 175.48° and 164.42°, respectively. The hydrogen bonds between O3 and O4 link the complex molecules to infinite one-dimensional chain along b, bipy molecules are parallel, however, π–π interactions do not occur because the distance of the neighboring planes is 7.442 Å (see figure 2b).

The crystal structure of $[CdHL(bipy)(H_2O)_2]_2 \cdot 2H_2O$ is shown in figure 1.3. Two Cd(II) ions are connected by two μ_2-bridging carboxyl oxygens. The Cd(II) is seven-coordinate via one water, one tridentate ligand (HL) and one bidentate bipy. The linkage of the ligands to Cd is accomplished through the acyl oxygen, carboxyl oxygen and imido nitrogen. Thus, two five-membered chelate rings sharing the same edges are formed. The coordination polyhedron of Cd(II) can be described as a distorted monocapped triangular prism. Atoms O(4), N(2), N(4) and O(9), O(3), N(3) form upper triangle plane and lower triangle plane, respectively, the angle between two planes is 5.3°, the capping atom is O(2) above the plane N(2), N(4), N(3), O(3) (see figure 2d). The Cd–O mean distance of 2.411 Å is comparable with the calculated average value 2.418 Å for Cd(II) complexes obtained with CONQUEST software from the Cambridge Structure Database (CSD) [34, 35]. Likewise, the Cd–N mean distance 2.338 Å is slightly lower than the calculated average value 2.347 Å for Cd(II) complexes using the data from the CSD.

In the complex, ligands coordinated in the keto form. In the same environment, the bond length of O(1)–C(5) of phenolic hydroxyl and O(6)–C(21) are 1.345 and 1.319 Å, respectively, the latter shorter than the former, showing electron density in the O(6)–C(21) bond is increased because of loss of hydrogen connected to O(6). The hydrogen bonds of O(6) with O(10), O(12) and N(6) are more extensive than those of O(1) with N(1), showing electron density of O(6) is increased after hydrogen loss and act as an electron donor. To the other tridentate ligand, the hydrogen in imine

N1 is lost, which not only makes the bond shorter because of a pair electrons on N1 transferred the bond C7–N1, but also balance the whole complex valence. So two *N*-(2-propionic acid)-salicyloyl hydrazones are coordinated with Cd^{2+} as dianion HL, but dehydrogenation mode of the two ligands is different, confirmed with IR and ^1H NMR. Association of the molecules in the crystal is dominated by hydrogen bonding, either between ligand molecules or involving the H_2O molecules. The main interactions are listed in table 9. Strong hydrogen bonds exist between coordinated water and uncoordinated O atoms (O(5)···O(10), 2.691 Å and the angle 171.13°; O(3)···O(8), 2.724 Å and the angle 156.66°). The binuclear units are bridged by two H_2O molecules via three hydrogen bonds to form a one-dimensional supermolecular chain along the crystallographic *a* axis. The distance of two adjacent bipy's (center-to-center) is 3.628 Å, the dihedral angle of the stacking pair was 1.3°, indicating the existence of the strong intermolecular π–π stacking interaction, stabilizing the 1D chain.

The crystal structure of $[NiHL(phen)H_2O]\cdot H_2O$ is shown in figure 1.4. The coordination environment is similar to **2**, substituting phen for bipy, and there being a crystal lattice water. The dihedral angle between chelation systems (L and phen) is 104.5°. The coordination polyhedron around Ni(II) is a distorted octahedron. The deviation from ideal geometry is due to strains induced by the tridentate (O, N, O), bidentate (N, N) and coordinated water molecule N1–Ni–N3 = 168.45(13)°, O3–Ni–O1 = 154.19(12)°, N2–Ni–O4 = 164.47(15)°, which cause a deviation 16° of the axial bond angle ∠N2NiO4 of the coordination octahedron. Due to chelation strain, the bond distances involving azomethine nitrogens (1.979–2.086 Å) are longer than those relative to pyridinic donors (1.959–1.965 Å) [30]. The bond length of O(3)–C(13) is 1.272(4) Å, indicating the ligand is keto form. Because of the chelation and hydrogen bond strains after coordination the planarity of the ligand is reduced. The phen is coplanar. There is intramolecular and intermolecular interaction. Intramolecular hydrogen bond interaction is between the phenolic hydroxy oxygen (O5) and imine nitrogen (N4) (O5–H···N4 = 2.538 Å and bond angle is 147.87°), while intermolecular interaction is between the coordinated water O4 and the crystal water O6, uncoordinated carboxylic oxygen O2 of the neighboring molecules at a distance O4–H···O6 = 2.710 Å, O4–H···O2 = 2.717 Å and bond angles are 161.48° and 170.57°, respectively. The hydrogen bond between crystal water O6 and coordinated carboxylic oxygen O1 is 2.733 Å. Phen of neighboring complexes are parallel, with shortest center-to-center distance of 3.436 Å, consistent with strong intermolecular π–π stacking (see figure 2e) [36]. Every molecule is linked with three

Table 9. Relevant intermolecular interactions of **3**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O12–H12D···O11[a]	0.92	1.91	2.757	152
O11–H11D···O8[b]	0.849	1.93	2.736	158
O10–H10A···O5	0.849	1.851	2.690	169
O10–H10B···O6[c]	0.847	1.853	2.695	172
O3–H3B···O11[d]	0.841	1.866	2.701	172
O3–H3A···O8	0.850	1.922	2.724	157
O1–H1A···N1	0.82	1.81	2.539	146.9
N6–H6···O6	0.86	1.81	2.524	139.3

Symmetry transformations used to generate equivalent atoms: [a]i: $x, y, z+1$; [b]ii: $-x+1, -y+1, -z$; [c]iii: $-x, -y+1, -z$; [d]iv: $x, y-1, z$.

neighboring molecules through six intermolecular H bonds and intermolecular π–π stacking interactions forming a 2D sheet along b (see figure 2d).

3.3. *Thermogravimetric analysis*

In order to examine the character of the water molecules and the thermal properties of the complexes, the weight loss and decomposition temperature were measured for **4** by thermogravimetric method. The TG-DTG curves show that the first weight loss of 3.58%, between 85 and 105°C, corresponds to the loss of an uncoordinated water molecule (Calcd: 3.64%), then lost 3.89% of its weight at 175–192°C, implying one water might be coordinated to Co ion. Further decomposition begins at 300°C and ends at 650°C with residue NiO in 14.82% yield (Calcd: 15.09%).

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 623328 for **1**, 623330 for **2**, 662540 for **3** and 623331 for **4**. Copies of this information may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ (Fax: +44 1223 336 033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the Natural Science Foundation of Shaanxi Province (2004B02), the breeding industrialized fund of the Education Committee of Shaanxi Province (06JC02) and the Xi'an Science Technology Bureau (GG06113).

References

[1] Z.F. Tian, Y. Su, J.G. Lin, Q.J. Meng. *Polyhedron*, **26**, 2829 (2007).
[2] Y. Xie, H.H. Wu, G.P. Yong, Z.Y. Wang, R. Fan, R.P. Li, G.Q. Pan, Y.C. Tian, L.S. Sheng, L. Pan, J. Li. *J. Mol. Struct.*, **833**, 88 (2007).
[3] S. Ianelli, G. Minardi, C. Pelizzi, L. Reverberri, C. Solinas, P. Tarasconi. *J. Chem. Soc., Dalton Trans.*, 2113 (1991).
[4] M. Bakir, I. Hassan, T. Johnson, O. Brown, O. Green, C. Gyles, M.D. Coley. *J. Mol. Struct.*, **688**, 213 (2004).
[5] D.G. Paschalidis, I.A. Tossidis, M. Gdaniec. *Polyhedron*, **19**, 2629 (2000).
[6] Z.Y. Yang, R.D. Yang, F.S. Li, K.B. Yu. *Polyhedron*, **19**, 2599 (2000).
[7] R.W. Deng, J.G. Wu, Z.N. Chen. *Synth. React. Met.-Org. Chem.*, **22**, 1295 (1992).
[8] W. Xiao, Z.L. Lu, C.Y. Su, K.B. Yu, L.R. Deng, H.Q. Liu, B.S. Kang. *J. Mol. Struct.*, **553**, 91 (2000).
[9] X.H. Bu, M. Du, L. Zhang, X.B. Song, R.H. Zhang, T. Clifford. *Inorg. Chim. Acta*, **308**, 143 (2000).
[10] P.K. Singh, B. Singh. *Indian J. Chem., Sect. A*, **37A**, 331 (1998).
[11] X. Shen, Y.Y. Xie, H.L. Jiang. *Synth. React. Inorg. Met.-Org. Chem.*, **25**, 511 (1995).
[12] M.X. Wang, H.Q. Den, W.D. Shan. *Chin. Chem. Lett.*, **2**, 587 (1991).
[13] S.Y. He, Y. Liu, J.S. Zhao, H.A. Zhao, R. Yang, R.Z. Hu, Q.Z. Shi. *Chin. J. Chem.*, **21**, 139 (2003).
[14] F.B. Tamboura, P.M. Haba, M. Gaye, A.S. Sall, A.H. Barry, T. Jouini. *Polyhedron*, **23**, 1191 (2004).

[15] M. Geraghty, V. Sheridan, M. McCann, M. Devereux, V. McKee. *Polyhedron*, **18**, 2931 (1999).

[16] J.L. Buss, E. Arduini, K.C. Shephard, P. Ponka. *Biochem. Pharmacol.*, **65**, 349 (2003).

[17] S.N. Pandeya, D. Siram, G. Nath, E. Declercq. *Eur. J. Pharm. Sci.*, **9**, 25 (1999).

[18] L.L. Koh, O.L. Kon, K.W. Long, J.D. Ranford, A.L.C. Tan, Y.Y. Tjan. *J. Inorg. Biochem.*, **72**, 155 (1998).

[19] S.Y. He, R. Yang, W.T. Wu, Q.Z. Shi, D.Q. Wang, D.R. An. *Chin. J. Chem.*, **23**, 1198 (2005).

[20] S.Y. He, W.K. Cao, J.L. Chen, J.S. Zhao, Q.Z. Shi, R.X. Wang, J. Sun. *Chem. J. Chin. Univ.*, **23**, 991 (2002).

[21] C. Wang, M. Zhao, J. Yang, X. Li, S. Peng. *Toxicol. Appl. Pharm.*, **200**, 229 (2004).

[22] O. Andersen. *Chem. Rev.*, **99**, 2683 (1999).

[23] D. Caiazza, S.F. Lincoln, A.D. Ward. *Inorg. Chem.*, **42**, 2531 (2003).

[24] D.S. Kumar, V. Alexander. *Inorg. Chim. Acta*, **63**, 238 (1995).

[25] D.G. Paschalidis, I.A. Tossidis, M. Gdaniec. *Polyhedron*, **19**, 2629 (2000).

[26] F.L. Yin, J. Shen, J.J. Zhou, R.C. Li. *Acta Chim. Sinica*, **61**, 556 (2003).

[27] N.S. Naraneetham, R. Lalyanasundaram, S. Soundararajan. *Inorg. Chim. Acta*, **110**, 169 (1985).

[28] W.J. Geary. *Coord. Chem. Rev.*, **7**, 81 (1971).

[29] S. Gao, Z. Shi, J. Hua, S.H. Feng, R.R. Xu, S.X. Liu, L.H. Huo, P.G. Chen. *Chem. J. Chin. Univ.*, **21**, 177 (2000).

[30] X.T. Wang, X.J. Han, W.J. Lu, X.W. Liu, D.C. Sun. *Synth. React. Inorg. Met.-Org. Chem.*, **22**, 1169 (1992).

[31] G. Singh, P.S.S.J. Shastry, R.K. Lonibala, T.R. Rao. *Synth. React. Inorg. Met.-Org. Chem.*, **22**, 1041 (1992).

[32] N. Kazuo. Translated by D.R. Huang, R.Q. Wang. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, p. 199, Chemical Industry Press, Beijing (1986).

[33] G. Pelizzi, A. Bacchi, I. Ivanovic-Burmazovic, M. Gruden, K. Andjelkovic. *Inorg. Chem. Commun.*, **4**, 311 (2001).

[34] F.H. Allen. *Acta Crystallogr. B*, **58**, 380 (2002).

[35] I.J. Bruno, J.C. Cole, P.R. Edington, M. Kessler, C.F. Macrae, P. McCabe, J. Pearson, R. Taylor. *Acta Crystallogr. B*, **58**, 389 (2002).

[36] Z.H. Liu, C.Y. Duan, J. Hu, X.Z. You. *Inorg. Chem.*, **38**, 1719 (1999).