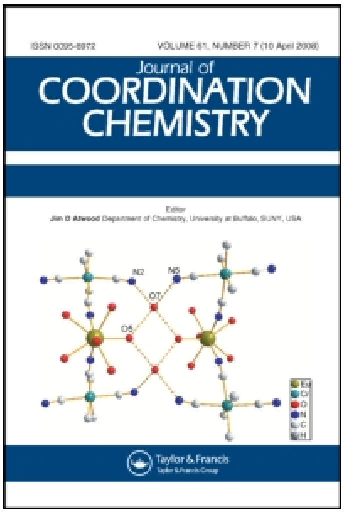

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1-D assembly of two metal complexes with aroylhydrazones and mono/bidentate heterocycles

Huiyan Liu[a]; Dezhong Niu[a]; Zaisheng Lu[a]
[a] School of Chemistry and Chemical Engineering, Xuzhou Normal University, Xuzhou, P.R. China

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1-D assembly of two metal complexes with aroylhydrazones and mono/bidentate heterocycles

HUIYAN LIU*, DEZHONG NIU and ZAISHENG LU

School of Chemistry and Chemical Engineering, Xuzhou Normal University,
Xuzhou 221116, P.R. China

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The two metal complexes, [NiL^1(Hdmpz)] (**1**) and [CuL^2(bipy)] · DMF (**2**), with substituted aroylhydrazones and N-donor heterocycle (Hdmpz) or a bidentate N,N-donor heterocycle (bipy) have been synthesized and structurally characterized. In the crystal lattice, each square-pyramidal [NiL^1(Hdmpz)] unit of **1** is connected to one neighbor by π–π and C–H–π interactions and to the other by a pair of C–H–π interactions, forming a chain-like arrangement of complexes with successive short and long Ni ··· Ni distances. In **2**, the two [CuL^2(bipy)] molecules link through a pair of Cu ··· Br contacts, forming a pseudodimer with each copper(II) displaying an elongated octahedron when the Br ··· Cu interaction is included. Each pseudodimer is further linked to another dimer via a pair of reciprocal hydrogen bonds, leading to a ladder-like chain arrangement.

Keywords: Self-assembly; Crystal structure; Hydrazone; Heterocycle

1. Introduction

A considerable effort is devoted to the investigation of extended transition metal ion complexes [1, 2] to generate new supramolecular entities by utilizing the metal ion's preference for different coordination geometries, designing suitable ligands, and using weak intermolecular interactions such as hydrogen bonding and π–π interactions [1–8]. Aroylhydrazones are potential ligands for construction of supramolecular frameworks due to several coordination sites [9, 10], as neutral or monoanionic bidentate or tridentate depending on the substituents and the reaction conditions. Furthermore, ability to coordinate to metals either in keto(I) or enol(II) tautomeric form make them attractive as ligands [10–20].

Pal *et al*. reported several square-planar nickel(II) and copper(II) complexes, [M(bhac)(hc)] (M = Ni, Cu), with an O,N,O-donor deprotonated Schiff base, acetylacetone benzoylhydrazone (H$_2$bhac), and a monodentate neutral N-donor heterocycle

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*Corresponding author. Email: liuhuiyan72@163.com

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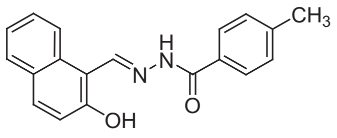
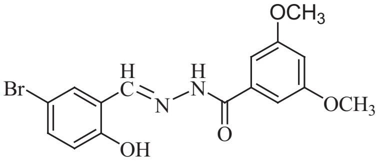
(hc = 3,5-dimethylpyrazole, pyrazole, imidazole, and pyridine) [14–16]. Self-assembly patterns of these analogous complexes are very different. The orientation of the phenyl ring plane in bhac^{2-} and that of the heterocycle ring plane with respect to the plane constituted by the rest of the molecules is significant for self-assembly and the resulting supramolecular structure [14–17].

In our previous work [21, 22], we have shown different supramolecular structures of copper(II) substituted aroylhydrazones with mono/bidentate heterocycles (hc = pyridine, imidazole, and 1,10-phenanthroline) as co-ligand. In this article, we examine the possible change in coordination behavior of the ligands and its concomitant effect on the solid state supramolecular assembly. Two metal complexes, [NiL^1(Hdmpz)] (**1**) and [CuL^2(bipy)] · DMF (**2**), with different structures using substituted aroylhydrazones (H_2L) and N-donor heterocycle (Hdmpz) or a bipy have been synthesized and structurally characterized. In the solid state, the self-assembly of **1** takes place through alternate pairs of π–π and C–H $\cdots$ π interactions, leading to a 1-D chain arrangement of nickel(II) ions. In **2**, a ladder-like chain is formed through successive pairs of Cu $\cdots$ Br contacts and hydrogen bonds.



H_2L^1



H_2L^2

2. Experimental

2.1. *Materials and physical measurements*

C, N, and H elemental analyses were carried out with a Varian EL elemental analyzer. IR spectra were recorded on a Bruker Tensor27 FT-IR spectrophotometer as KBr pellets. Electronic spectra were recorded on a Shimadzu 2500PC spectrophotometer. The substituted aroylhydrazones, H_2L^1 and H_2L^2, were prepared by condensation of substituted benzoylhydrazine with 2-hydroxy-naphthaldehyde and 5-bromo-salicylaldehyde in methanol, respectively. All other chemicals and solvents used were of analytical grade, available commercially and used without purification.

2.2. *Synthesis*

2.2.1. [NiL^1(Hdmpz)] (1). To a mixed solution of methanol (10 cm^3) and DMF (5 cm^3) of H_2L^1 (0.06 g, 0.2 mmol) and 3,5-dimethylpyrazole (Hdmpz) (0.07 g, 0.6 mmol), a methanol solution (8 cm^3) of $Ni(O_2CCH_3)_2 \cdot 4H_2O$ (0.05 g, 0.2 mmol) was added gradually with stirring. The resulting red solution was further stirred for 2 h and filtered. Reddish brown crystals separated after about two weeks were collected. Yield: 60%. Anal. Calcd for $C_{24}H_{22}N_4NiO_2$ (%): C, 63.06; N, 12.26; H, 4.85. Found (%): C, 63.35; N, 11.92; H, 4.96.

2.2.2. [CuL^2(bipy)] · DMF (2). This complex was synthesized in 75% yield and isolated as greenish brown crystalline material in the same manner as detailed for **1** by reacting H_2L^2, $Cu(O_2CCH_3)_2 \cdot H_2O$ and 2,2′-bipyridine (1 : 1 : 3 mole ratio) in a mixed solution of methanol and DMF. Anal. Calcd for the desolvated species $C_{26}H_{21}BrCuN_4O_4$ (%): C, 52.31; N, 9.39; H, 3.55. Found (%): C, 52.64; N, 9.26; H, 3.45.

2.3. *Crystal structure determination*

Diffraction data of **1** and **2** were collected on a Bruker Smart-1000 CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 298(2) K. Both structures were solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for all nonhydrogen atoms. All hydrogens were located geometrically and refined isotropically. For **2**, C27, C28, and C29 of DMF were disordered over two positions, with site occupation factors of 0.744/0.256. Data collection and refinement details for **1** and **2** are summarized in table 1.

Table 1. Crystallographic data for **1** and **2**.

	1	**2**
Empirical formula	$C_{24}H_{22}NiN_4O_2$	$C_{29}H_{28}BrCuN_5O_5$
Formula weight	457.17	670.01
Crystal system	Monoclinic	Monoclinic
Space group	*P 2(1)/n*	*P 2(1)/c*
Unit cell dimensions (Å, °)		
a	11.0540(15)	12.5955(16)
b	8.0134(12)	23.684 (3)
c	23.695(3)	9.6358(11)
α	90	90
β	93.298(2)	100.255(2)
γ	90	90
Volume (Å^3), *Z*	2095.5(5), 4	2828.6(6), 4
Calculated density (mg m^{-3})	1.449	1.573
Absorption coefficient (mm^{-1})	0.955	2.233
F(000)	952	1364
θ range for data collection (°)	1.72–25.01	1.64–25.02
Limiting indices	$-12 \le h \le 13$; $-9 \le k \le 9$; $-28 \le l \le 23$	$-14 \le h \le 13$; $-28 \le k \le 26$; $-11 \le l \le 11$
Reflection collected	10231	14251
Independent reflection	3656 [R(int) = 0.0415]	4976 [R(int) = 0.0469]
Completeness to $\theta = 25.00$ (%)	99.0	99.7
Max. and min. transmission	0.7498/0.6732	0.8777/0.5944
Reflections with $[I > 2\sigma(I)]$	2811	3559
Data/restraints/parameters	3656/0/280	4976/0/398
Goodness-of-fit on F^2	1.172	1.029
Final *R* indices $[I > 2\sigma(I)]$	$R_1 = 0.0546$, $wR_2 = 0.1070$	$R_1 = 0.0425$, $wR_2 = 0.0840$
R indices (all data)	$R_1 = 0.0775$, $wR_2 = 0.1175$	$R_1 = 0.0724$, $wR_2 = 0.0935$
Largest difference peak and hole (e Å^{-3})	0.412 and −0.273	0.489 and −0.516

3. Results and discussion

3.1. *Synthesis*

The complexes have been synthesized by reacting 1 mol equivalent of H_2L and metal(II) acetate and 3 mol equivalents of the corresponding heterocycle. In each case, the metal ion solution was added to the solution of a mixture of H_2L and excess heterocycle to prevent precipitation of the insoluble dimeric species commonly obtained with similar tridentate dibasic ligands [14, 17–19].

3.2. *IR spectra and electronic spectra*

IR spectrum of **1** displays a strong band at 3281 cm^{-1}, associated with Hdmpz N–H [15, 17]. The spectrum of **2** is devoid of a band in this region. None of the spectra display a band assignable to C=O of the amide present in the tridentate Schiff base at ca 1650 cm^{-1}. This observation is consistent with deprotonation and the enolate form of the amide in each complex [11, 12]. A strong band attributed to conjugated C=N–N=C is observed at 1618 cm^{-1} for **1** and 1605 cm^{-1} for **2** [15, 17, 21, 22].

The electronic spectrum of **1** shows bands at 322, 331, 376, 421, and 442 nm. The electronic spectrum of **2** shows bands at 320, 336, and 400 nm. The strong absorptions between 320 and 376 nm can be assigned to intraligand transition, and the strong absorption band at ca 400 nm may correspond to the ligand-to-metal charge transfer [15, 17, 21, 22].

3.3. *Crystal structure of 1*

A perspective view of **1** with the labeling scheme is given in figure 1 and selected bond parameters are listed in table 2. The nickel(II) is square-planar N_2O_2 formed by the phenolate-O, the imine-N and the deprotonated amide-O of L^{2}-, and the imine-N of Hdmpz. The C1–O1 (1.313(4) Å) and N1–C1 (1.301(5) Å) distances are consistent with the enolate form of the amide [15–17]. The Ni–O(amide) (1.844(2) Å) and Ni–N(imine) (1.815(3) Å) distances (table 2) are comparable to those observed in other nickel(II) complexes with aroylhydrazones [16, 23]. The Ni–O(phenolate) distance (1.828(3) Å) is comparable to those reported for nickel(II) complexes having the same coordinating atoms [16, 23]. The Ni–N(pyrazole) bond distance is comparable to the distance observed in another tetracoordinated Ni(II) complex containing monodentate neutral pyrazole moiety [16].

There is no displacement of nickel from the N_2O_2 square plane. The maximum and minimum deviations from the NiN_2O_2 mean plane are 0.0158 and 0.0002 Å for N2 and Ni1, respectively. In the {NiL} fragment, the Ni1, O1, O2, N1, N2, C1, and C9–C19 atoms are planar (mean deviations are in the range 0.0057–0.0644 Å). However, the phenyl ring plane of the benzoyl fragment is twisted with respect to the above mentioned plane. The dihedral angle between these two planes is 11.94(1)°. In addition, the heterocycle ring plane also has a different orientation with respect to the plane containing Ni1, O1, O2, N1, N2, C1, and C9–C19. The dihedral angle between these two planes is 8.15(2)°.

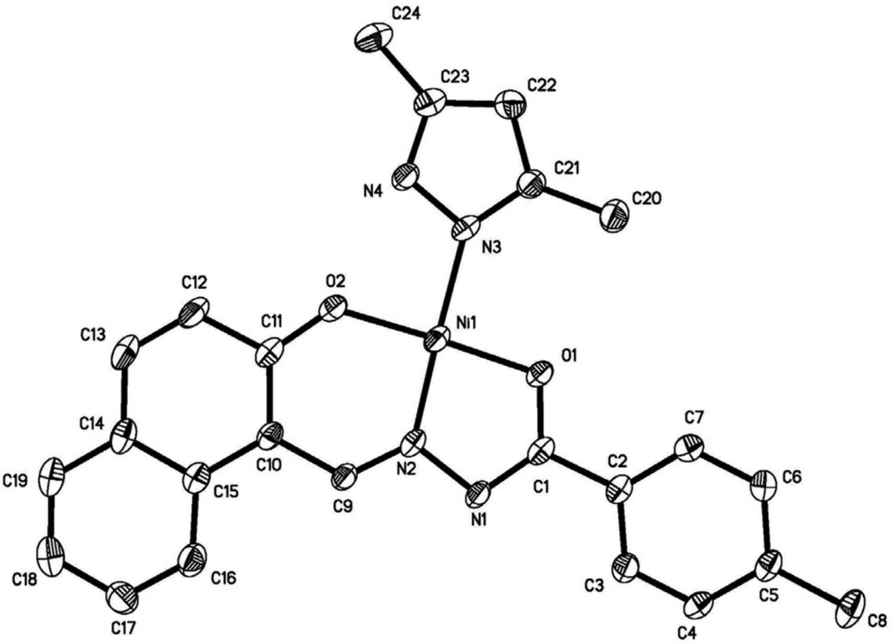


Figure 1. Structure of [NiL^1(Hdmpz)] (**1**) with the atom labeling scheme.

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

Ni(1)–O(1)	1.844(2)	Ni(1)–O(2)	1.828(3)
Ni(1)–N(2)	1.815(3)	Ni(1)–N(3)	1.938(3)
N(1)–C(1)	1.301(5)	O(1)–C(1)	1.313(4)
N(2)–Ni(1)–O(2)	93.70(12)	N(2)–Ni(1)–O(1)	83.96(12)
O(2)–Ni(1)–O(1)	177.47(12)	N(2)–Ni(1)–N(3)	178.07(13)
O(2)–Ni(1)–N(3)	88.00(13)	O(1)–Ni(1)–N(3)	94.36(12)
C(1)–N(1)–N(2)	106.8(3)	C(9)–N(2)–N(1)	115.3(2)
C(9)–N(2)–Ni(1)	129.0(3)	N(1)–N(2)–Ni(1)	115.7(2)

In the crystal lattice, each molecule is involved in π–π and C–H–π interactions (figure 2). The Hdmpz rings and the six-membered chelate rings {Ni1, N2, O2, C9–C11} of two molecules are involved in π–π interactions in a reciprocal manner. The interplanar and centroid-to-centroid distances are 3.2097 and 3.6881 Å, respectively. In addition, the methyl C–H groups on Hdmpz and the naphthaldehyde ring {C10–C15} of these two molecules are also involved in C–H–π interactions. The H20C $\cdots$ cg distance and C20–H20C $\cdots$ cg angle are 2.77 Å and 145°, respectively. Thus, two molecules form dimeric units due to these interactions. The Ni $\cdots$ Ni distance in this dimeric unit is 3.4804 Å. Methyl C–H groups on Hdmpz of each of these dimeric units are involved in other C–H–π interactions with the naphthaldehyde ring (C14–C19) of neighboring dimers and the interdimer Ni $\cdots$ Ni distance observed is 5.5409 Å. The H20A $\cdots$ cg distance and C20–H20A $\cdots$ cg angle are 2.67 Å and 172°, respectively. As a consequence, there are sequential short (3.4804 Å) and long

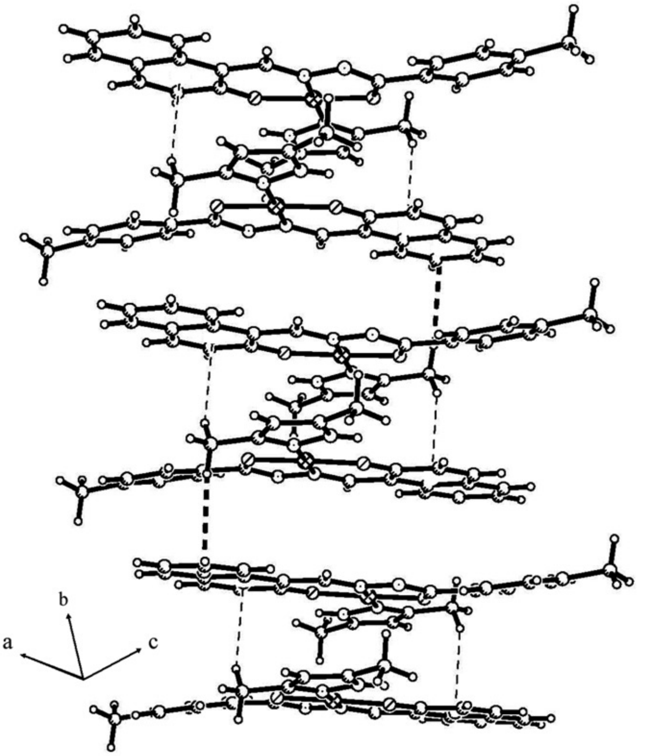


Figure 2. 1-D chain arrangement of [NiL^1(Hdmpz)] (**1**) in the crystal lattice.

(5.5409 Å) Ni $\cdots$ Ni distances in the chain-like arrangement of the metal ions. There are no significant interchain short contacts or noncovalent interactions.

Comparing the π-stacked 1-D arrangement of present complex with hydrogen-bonded dimer formation of [Ni(bhac)(Hdmpz)] (H_2bhac = acetylacetone benzoylhydrazone) [16] shows the dihedral angles between the phenyl ring plane and the heterocycle ring plane, and the plane constituted by rest of the molecules are 34.4(1)° and 69.12(7)°, respectively, in [Ni(bhac)(Hdmpz)], while in our complex, the values are 11.94(1)° and 8.15(2)°. Apparently, this difference in orientation of the phenyl ring plane and heterocycle ring plane may be responsible for the π-stacked 1-D arrangement of **1** and dimer formation for [Ni(bhac)(Hdmpz)] via hydrogen bonds.

3.4. *Crystal structure of 2*

The molecular structure of **2**, together with the atom numbering scheme is illustrated in figure 3 and selected bond parameters are listed in table 3. The asymmetric unit of **2** contains the complex and a DMF.

Copper(II) is in a distorted square pyramid. The basal coordination positions are occupied by the phenolate O4, the imine N2, and the deprotonated amide O1 of L^{2-}, and N3 of bipy. The apical position is occupied by N4 of bipy. The ligands form a O_2N_2 square plane around copper, with the largest deviation from the mean plane of 0.0900 Å

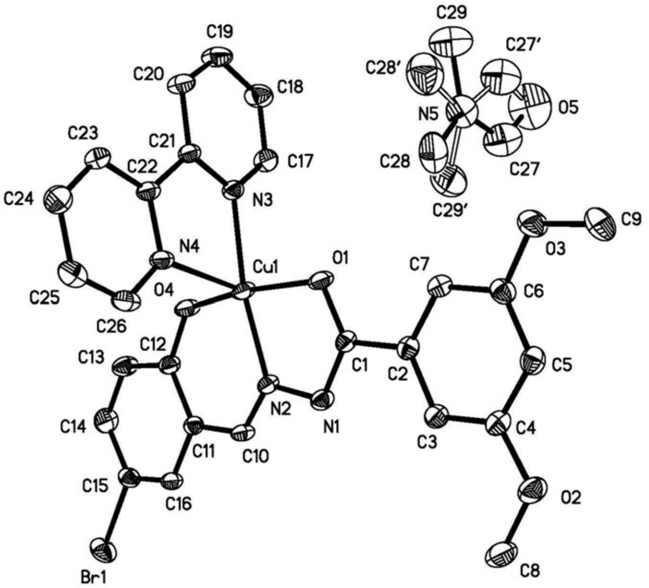


Figure 3. Structure of $[CuL^2(bipy)] \cdot DMF$ (**2**) with the atom labeling scheme.

Table 3. Selected bond distances (Å) and angles (°) for **2**.

Cu(1)–O(1)	1.975(2)	Cu(1)–O(4)	1.928(2)
Cu(1)–N(2)	1.923(3)	Cu(1)–N(3)	2.052(3)
Cu(1)–N(4)	2.265(3)	O(1)–C(1)	1.293(4)
N(1)–C(1)	1.323(4)		
N(2)–Cu(1)–O(4)	92.71(11)	N(2)–Cu(1)–O(1)	81.18(11)
O(4)–Cu(1)–O(1)	167.63(11)	N(2)–Cu(1)–N(3)	171.02(13)
O(4)–Cu(1)–N(3)	91.06(10)	O(1)–Cu(1)–N(3)	93.54(10)
N(2)–Cu(1)–N(4)	111.42(11)	O(4)–Cu(1)–N(4)	98.76(11)
O(1)–Cu(1)–N(4)	93.50(10)	N(3)–Cu(1)–N(4)	75.99(11)

for N2. As commonly observed in square pyramidal complexes, the copper is displaced by 0.1294 Å from the basal plane towards the apical N4. The axial Cu1–N4 (2.265(3) Å) bond length is longer than equatorial Cu1–N3 (2.052(3) Å) and Cu–N2 (1.923(3) Å) bond lengths. Bond angles of O1–Cu1–N4 (93.50(10)°), N2–Cu1–N4 (111.42(11)°) and N3–Cu1–N4 (75.99(11)°) indicate distortion from perfect square-pyramidal geometry. The Cu–O and Cu–N distances are comparable to the distances observed in other copper(II) complexes having the same coordinating atoms [24].

In this complex, L^{2-} also adopts the enolate form bonded to Cu1. The C1–O1 (1.293(4) Å) and N1–C1 (1.323(4) Å) distances are consistent with the enolate form of the amide [15–17]. Dihedral angles between the phenyl ring plane and the plane constituted by Cu1, O1, O4, N1, N2, and C10–C16 (mean deviations are in the range 0.0065–0.1419 Å) is 5.23(9)°. The dihedral angle between bipy and the above mentioned plane is 86.61(6)°.

Complex **2** has a unique self-assembly shown in figure 4. The two $[CuL^2(bipy)]$ molecules link through a contact between bromide and copper with a distance of

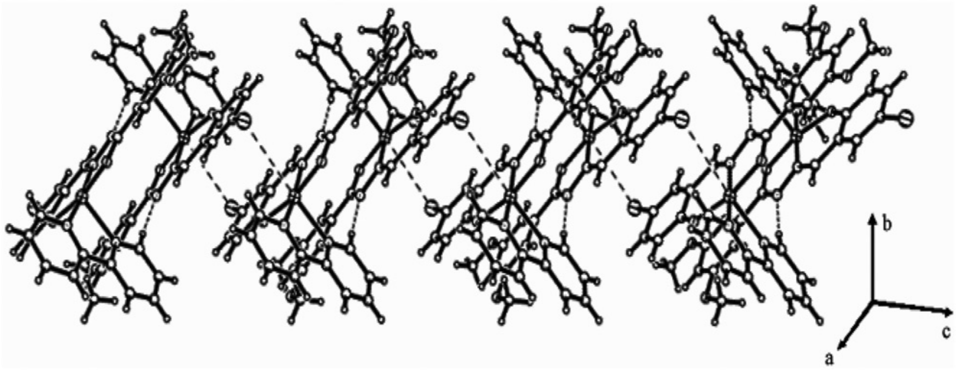


Figure 4. 1-D ladder-like arrangement of $[CuL^2(bipy)] \cdot DMF$ (**2**) in the crystal lattice. Disordered DMF molecules are not shown for clarity.

3.5818 Å, creating a pseudodimer with each copper(II) displaying elongated octahedral coordination geometry when the Br ··· Cu interaction is included. The Cu ··· Br contact (3.5818 Å) is shorter than that observed in other complexes (4.1512–4.1547 Å) [25]. Within this dimer the Cu ··· Cu distance is 8.4911(9) Å. Each pseudodimer further links to another dimer via a pair of reciprocal hydrogen bonds between bipy C–H and the uncoordinated and deprotonated amide-N. The C ··· N distance and C–H ··· N angle are 2.775 Å and 162.85°, respectively. The Cu ··· Cu distance in the dimeric fragment formed by hydrogen bonds is 6.8666 Å. Thus, a ladder-like chain is formed through successive pairs of Cu ··· Br contacts and hydrogen bonds (figure 4). This unique self-assembly is not observed in $[CuL(phen)] \cdot 0.5DMF$ (H_2L = 5-bromo-salicylaldehyde-3,5-dimethoxy-benzoylhydrazone), in which a 1-D assembly is formed by hydrogen bonds between the phenyl ring C–H group of one molecule and the methoxy substituent of an adjacent molecule [22].

Supplementary material

CCDC 730688 and 730689 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 Email: deposit@ccdc.cam.ac.uk

Acknowledgments

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