

# A series of 3d metal complexes prepared by in situ reactions of a flexible diacylhydrazine ligand: synthesis, structures and magnetic properties

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Abstract The coordination reactions of 3d metal salts with malonic acid N, N'-bis(salicyloyl) bishydrazide (H<sub>6</sub>mbshz) afforded three complexes, namely  $[Cu_2(H_2bshz)(Py)_4Cl_2]$ .  $Py (1) (Py = pyridine), [Fe_2(bshz)(Py)_2] (2)$  and the known complex  $[Ni_4(aehba)_2(DMF)_2(H_2O)_2] \cdot 2DMF$  (3), where  $bshz = N, N'-bis(salicyloyl)hydrazine anion and aehba^{4-} =$ azo-enolic-2-hydroxybenzamide anion. The X-ray crystal structures of all three complexes have been obtained. Complexes 1 and 2 are composed of N-N-bridged binuclear units, while complex 3 displays a planar tetranuclear structure in which four Ni(II) centers are linked together by N-N and N=N bonds. The bshz anions in 1 and 2 and  $aehba^{4-}$  anions in 3 were all generated in situ from H<sub>6</sub>mbshz. A mechanism for these reactions is proposed, involving tandem C-N cleavage and C-N/N-N coupling processes via free radical intermediates. Magnetic investigations revealed dominant antiferromagnetic interactions between the metallic centers of each complex.

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## Introduction

The reactions of metal ions with ligands formed in situ from pro-ligands are effective in the synthesis of novel complexes and serve as an alternative to the more generally employed coordination reactions of metal ions with presynthesized ligands [1, 2]. Although it is difficult to predict the final structures of such products, a number of sophisticated coordination assemblies which are difficult to synthesize through routine methods can thus be made accessible and some of these have been found to possess interesting structures and promising properties [3, 4]. For example, a rare pillar-layered homochiral metal organic framework with X-shaped pillars and zinc paddle wheels was obtained through the in situ reaction of D-camphorate [4], while two Cu–Ln nanomagnets were synthesized via a two-step in situ reaction of picolinaldehyde [5]. On the other hand, such in situ reactions also open a new avenue toward the discovery of novel organic reactions and facilitate the elucidation of reaction mechanisms, acting as a bridge between coordination chemistry and organic chemistry [6]. A variety of interesting organic reaction processes have been observed during in situ reactions, such as oxidative hydroxylation of aromatic rings [7, 8], dehydrogenative C-C couplings [9], cycloaddition of organic nitriles with azides and ammonia [10-12] and the transformation of inorganic and organic sulfur [13].

In recent years, our group has been interested in the coordination chemistry of diacylhydrazine ligands [14–16]. These ligands take advantage of multiple chelating pockets and variable coordination modes. In particular, we have investigated the influence of their structures on the architectures and properties of the resulting complexes, obtained by variations of the substituents and terminal groups on their core structures. In continuation of our previous work,

we have employed flexible malonic acid as a core scaffold for the synthesis of a new pro-ligand, N,N'-bis(salicyloyl) bishydrazide (H<sub>6</sub>mbshz), and set out to study its coordination chemistry with 3d metal ions. Interestingly, the reactions of 3d metal salts with H<sub>6</sub>mbshz resulted in three complexes, in which the H<sub>6</sub>mbshz was transformed to N,N'-bis(salicyloyl)hydrazine (bshz) ligands in 1 and 2 and azo-enolic-2-hydroxybenzamide (aehba<sup>4-</sup>) ligand in 3, respectively. Herein, we report the synthesis and crystal structures of all three complexes. A mechanism for the in situ ligand formation reactions is proposed, and the magnetic properties of the complexes are also described.

# Experimental

## Materials and methods

All reagents were used as received without further purification. IR spectra were recorded in the range of 4000-400 cm<sup>-1</sup> on a Perkin-Elmer Spectrum One FT/IR spectrometer using KBr pellets. Elemental analyses for C, H and N were obtained on a Model 2400 II, Perkin-Elmer elemental analyzer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AV 400 spectrometer at 400 and 100 MHz, respectively. The ESI mass spectra were acquired using a Bruker Daltonics HCT mass spectrometer. Magnetic susceptibility measurements were taken in the temperature range of 300-2 K using a Quantum Design MPMS SOUIDXL-5 magnetometer equipped with a 5-T magnetic field. The diamagnetic corrections for the complexes were estimated using Pascal's constants, and magnetic data were corrected for diamagnetic contributions of the sample holder.

#### X-ray structure determinations

All the data for complexes 1-3 were collected with a Bruker SMART CCD instrument using graphite monochromatic Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The data were collected at 153.15 K for 1 and 3 and at 296.15 for 2. Absorption effects were corrected by semiempirical methods. The structures were solved by direct methods and were refined by full-matrix least-squares methods with the SHELXL-2013 crystallographic software package [17–19] and Olex2 [20]. The non-hydrogen atoms were refined anisotropically. The aromatic hydrogen atoms were placed in calculated positions and refined using a riding model, while other hydrogen atoms were located in the last final difference Fourier map. The final cycle of full-matrix leastsquares refinement was based on observed reflections and variable parameters. A summary of crystal data and relevant refinement parameters for these complexes is given in Table 1. Selected bond lengths and bond angles are given in Table S1.

# Synthesis of malonic acid N', N'-bis(salicyloyl) bishydrazide (H<sub>6</sub>mbshz)

A solution of malonyl dichloride (2 mL) in THF (15 mL) was added slowly to a solution of triethylamine (2.8 mL) and salicylhydrazide (7.2 g, 50 mmol) in THF (60 mL) at 0 °C. The resulting mixture was slowly warmed to ambient temperature and was further stirred for 24 h. A reddish brown oil was obtained after filtration and concentration. The recrystallization of the oil-like crude product in DMF-H<sub>2</sub>O gave H<sub>6</sub>bsbhz as a yellow precipitate in 75 % yield. IR (KBr, cm<sup>-1</sup>): 3453 (s, br), 3282 (vs), 1719 (m), 1662 (vs), 1640 (vs), 1604 (vs), 1552 (m), 1493 (vs), 1455 (m), 1351 (m), 1313 (m), 1245 (m), 1212 (m), 1164 (m), 756 (s), 735 (m), 526 (w). Elemental analysis (%) calcd.: C, 54.84; H, 4.33; N, 15.05; Found: C, 54.66; H, 4.70; N, 15.24. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ):  $\delta = 11.88$  (s, 2H), 10.72 (s, 2H), 10.51 (s, 2H), 7.91 (d, 2H, J = 7.9 Hz), 7.45 (m, 2H), 6.95  $(m, 4H), 3.38 (s, 2H) ppm; {}^{13}C NMR (100 MHz, DMSO-d_6):$  $\delta = 166.59, 164.94, 159.21, 134.56, 129.10, 119.63, 117.74,$ 115.18, 40.59 ppm. ESI-MS m/z:  $373.15 \text{ [M + H]}^+$ .

## Synthesis of complex 1

A mixture of  $H_6$ mbshz (0.76 g, 0.2 mmol) and CuCl<sub>2</sub>-6H<sub>2</sub>O (0.120 g, 0.6 mmol) in Py (10 mL) was refluxed at 70 °C for 6 h followed by filtration. The filtrate was left to evaporate at ambient temperature, giving light blackish green crystals of complex **1** [Cu<sub>2</sub>(H<sub>2</sub>bshz)(Py)<sub>4</sub>Cl<sub>2</sub>]·Py suitable for X-ray analysis after 1 week. Yield: 35 % (based on Cu<sup>2+</sup>). IR (KBr, cm<sup>-1</sup>): 3420 (m, br), 3069 (m), 1602 (s), 1553 (s), 1516 (m), 1463 (vs), 1397 (s), 1334 (m), 1255 (s), 1222 (m), 1145 (m), 1082 (m), 1040 (s), 913 (m), 853 (m). Elemental analysis (%) calcd.: C, 54.23; H, 4.08; N, 11.35 %. Found: C, 54.43; H, 3.92; N, 11.29 %.

# Synthesis of complex 2

A mixture of H<sub>6</sub>mbshz (0.19 g, 0.05 mmol) and FeCl<sub>3-</sub> 6H<sub>2</sub>O (0.540 g, 0.2 mmol) in a mixture of MeOH and Py (2.0 mL, V/V = 1/1) was sealed in a Pyrex tube, heated to 80 °C for 72 h and then cooled to room temperature at a rate of 0.5 °C min<sup>-1</sup>. Blackish rhombohedral crystals of complex **2** [Fe<sub>2</sub>(dshz)<sub>2</sub>(Py)<sub>2</sub>] suitable for X-ray analysis were obtained after one week. Yield: 39 % (based on Fe<sup>3+</sup>). IR (KBr, cm<sup>-1</sup>): 3416 (m, br), 1638 (s), 1597 (s), 1561 (m), 1498 (vs), 1445 (s), 1403 (m), 1321 (s), 1261 (m), 1215 (m), 1152 (m), 1088 (s), 760 (m), 690 (m). Elemental analysis (%) calcd.: C, 58.65; H, 4.05; N, 12.07; Found: C, 58.39; H, 4.17; N, 12.14.

Table 1Crystal data andstructure refinement parametersfor 1-3

Identification code	1	2	3
Empirical formula	C <sub>39</sub> H <sub>35</sub> Cl <sub>2</sub> N <sub>7</sub> O <sub>4</sub> Cu <sub>2</sub>	C <sub>68</sub> H <sub>56</sub> N <sub>12</sub> O <sub>8</sub> Fe <sub>4</sub>	C40H48N12O14Ni4
Formula weight	863.72	1392.65	1155.74
Temperature/K	153.15	296.15	153.15
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> /c	<i>P</i> 2 <sub>1</sub> /n	<i>P</i> 2 <sub>1</sub> /c
a/Å	17.9260(3)	16.8207(4)	8.8437(18)
b/Å	10.8903(2)	11.4918(2)	14.410(3)
c/Å	19.7967(3)	17.6341(4)	19.982(6)
β/°	98.3990(10)	114.036(3)	116.27(2)
V/Å <sup>3</sup>	3823.25(11)	3113.11(12)	2283.5(10)
Ζ	4	2	2
$D_c/\mathrm{g}~\mathrm{cm}^{-3}$	1.501	1.486	1.681
$\mu/mm^{-1}$	1.303	0.981	1.704
<i>F</i> (000)	1768	1432.0	1192.0
Reflections collected	16,166	22,482	16,545
Independent reflections	6717	5377	4029
Data/restrains/parameters	6717/3/499	5377/1/415	4029/6/350
<i>R</i> <sub>int</sub>	0.0267	0.0361	0.0351
GOF	1.068	1.028	1.048
Final <i>R</i> indexes $(I > 2\sigma(I))$	$R_1 = 0.0639$	$R_1 = 0.0604$	$R_1 = 0.0309$
	$wR_2 = 0.1852$	$wR_2 = 0.1403$	$wR_2 = 0.0701$
Final <i>R</i> indexes (all data)	$R_1 = 0.0755$	$R_1 = 0.0731$	$R_1 = 0.0386$
	$wR_2 = 0.1970$	$wR_2 = 0.1509$	$wR_2 = 0.0752$

# Synthesis of complex 3

A mixture of H<sub>6</sub>mbshz (0.19 g, 0.05 mmol) and Ni(OAc)<sub>2</sub>-H<sub>2</sub>O (0.250 g, 0.1 mmol) in a mixture of DMF, MeOH and Py (4.5 mL, V/V = 7/1/1) was sealed in a stainless steel vessel, heated to 80 °C for 72 h and then cooled to room temperature at a rate of 0.5 °C min<sup>-1</sup>. The filtrate was left to evaporate at ambient temperature, giving red brown crystals of complex **3** [Ni<sub>4</sub>(aehba)<sub>2</sub>(DMF)<sub>2</sub> (H<sub>2</sub>O)<sub>2</sub>]·2DMF suitable for X-ray analysis after one week. Yield: 27 % (based on Ni<sup>2+</sup>). IR (KBr, cm<sup>-1</sup>): 3374 (m, br), 1659 (s), 1598 (s), 1551 (m), 1528 (vs), 1465 (s), 1360 (m), 1254 (s), 1152 (m), 1102 (m), 1033 (m), 1002 (s), 835 (m), 759 (m). Elemental analysis (%) calcd.: C, 41.57; H, 4.19; N, 14.54; Found: C, 41.60; H, 4.26; N, 14.61.

# **Results and discussion**

# X-ray crystal structures of the complexes

Single-crystal X-ray diffraction studies reveal that complexes 1-3 all crystallize in the monoclinic space group  $P2_1/c$ . Complex 1 was obtained from the evaporation of a pyridine solution of H<sub>6</sub>mbshz and CuCl<sub>2</sub> at ambient temperature. Its molecular structure contains two Cu(II) centers, a H<sub>2</sub>bshz<sup>2-</sup> ligand generated in situ, two coordinated Cl<sup>-</sup> anions, plus two coordinated and one free Py (Fig. 1). Atom Cu1 adopts a distorted octahedral CuN<sub>3</sub>O<sub>2</sub>Cl geometry, whose four equatorial positions are occupied by a phenolic oxygen atom (O1), an acyl oxygen atom (O3), an acylhydrazine nitrogen atom (N1) and a chloride ligand (Cl1), respectively. The axial positions are occupied by two Py nitrogen atoms (N3 and N4). The geometry of Cu2 is almost the same as that of Cu1, only differing in the bond distances and angles. The H2bshz2- ligand is not completely deprotonated, carrying a charge of -2 according to charge balance calculations. This result is further supported by the presence of a peak of  $3069 \text{ cm}^{-1}$  in the IR spectrum of the complex, which can be ascribed to the O-H stretching vibrations of the phenol groups (Fig. S1). The  $H_2bshz^{2-}$  ligand adopts an  $\eta^6$ - $\mu_2$  coordination mode, in which all of the available donors are used to provide two chelating pockets around the Cu<sup>2+</sup> ions, such that an N-N bond-bridged dinuclear structure is formed, as shown in Fig. 1. The Cu-O and Cu-N bond distances fall in the ranges of 1.901(3)-2.041(3) and 2.061(4)-2.213(4) Å, respectively. The torsion angle Cu1-N-N-Cu2 is 179.0°,



Fig. 1 Molecular structure of 1. Selected geometric data: Cu(1)–Cl(1) 2.2886(13); Cu(1)–N(1) 2.061(4); Cu(2)–N(2) 2.062(4); Cu(1)–N(3) 2.213(4); Cu(1)–N(4) 2.200(4); Cu(1)–O(1) 1.901(3); Cu(1)–O(3) 2.019(3); Cu(2)–Cl(2) 2. 297(13); Cu(2)–N(5) 2.183(4); Cu(2)–N(6) 2.206(4); Cu(2)–O(2) 2.041(3); Cu(2)–O(4) 1.909(3) Å. O(1)–Cu(1)–N(1) 85.52(15); O(3)–Cu(1)–N(1) 76.49(14); N(1)–Cu(1)–Cl(1) 171.82(12); N(1)–Cu(1)–N(3) 88.66(15); N(1)–Cu(1)–N(4) 89.93(15); O(2)–Cu(2)–N(2) 76.44(14); O(4)–Cu(2)–N(2) 85.28(14); N(2)–Cu(2)–Cl(2) 172.99(12); N(2)–Cu(2)–N(5) 89.29(15); N(2)–Cu(2)–N(6) 88.58(15)°

and the Cu1...Cu2 distance is 4.874 Å. All these structural parameters are comparable to those of complexes with similar structures [21–23]. A weak hydrogen bond (C28–H28...Cl1: 2.810 Å) exists between the neighboring {Cu<sub>2</sub>} units, linking them to form supermolecular chains expanding along the *c*-axis (Fig. 2).

The solvothermal reaction between H<sub>6</sub>mbshz and FeCl<sub>3</sub> in methanol–pyridine mixed solvent gave complex **2**, in which the bshz<sup>4–</sup> ligand generated in situ shows the same  $\eta^6-\mu_2$  mode as that of H<sub>2</sub>bshz<sup>2–</sup> in **1**. However, the molecular structure of complex **2** contains two very similar but discrete dinuclear units, both of which are composed of a bshz<sup>4–</sup> ligand, two Fe centers and four Py ligands (Fig. 3). Both Fe centers are in the +2 oxidation state, as established by bond valence sum (BVS) calculations and charge balance considerations. They both show five-coordinated FeN<sub>3</sub>O<sub>2</sub> geometries, in which the basal planes are provided by a phenol oxygen atom (O1 or O3), an acyl oxygen atom (O3 or O4), an acylhydrazine nitrogen atom (N1 or N2) and a Py nitrogen atom (N3 or N5). The apical position is occupied by another Py nitrogen atom (N4 or N6). The geometrical parameter  $\tau = (\beta - \alpha)/60$  was calculated to evaluate the coordination geometries of the Fe(II) centers, where  $\beta$  and  $\alpha$  represent the two largest ligand–metal–ligand bond angles [24, 25]. The resulting  $\tau$ values for Fe1 and Fe2 are 0.23 and 0.19, respectively, indicating square pyramidal geometries in both cases. The ranges of the Fe-O and Fe-N bond distances are 1.918(4)-1.949(4) and 1.913(4)-2.306(4) Å, respectively. The Fe-N-N-Fe torsion angles are both 180.0°, while the Fe1…Fe1 and Fe2...Fe2 distances are 4.551 and 4.565 Å, respectively. These structural data are close to those of a previously reported  $\{Cu_2\}$  complex [26], which was constructed directly from H<sub>4</sub>bshz ligands.

Complex 3 was synthesized through the reaction of H<sub>6</sub>mbshz with Ni(OAc)<sub>2</sub> in the presence of Py in DMFmethanol solvent mixture. Instead of formation of the bshz ligand, H<sub>6</sub>mbshz was transformed to aehba<sup>4-</sup> in situ in this experiment. As shown in Fig. 4, the molecule of complex 3 possesses a planar tetranuclear  $\{Ni_4\}$  structure in which four Ni centers are linked together through N-N and N=N bonds. Two  $\eta^8$ - $\mu_3$  aehba<sup>4-</sup> ligands are nearly coplanar. Each of them chelates a Ni1 center and employs their N=N bonds to bridge two Ni2 ions. The Ni1 ions have square planar geometries, while the Ni2 atoms are distorted octahedral, with DMF and H<sub>2</sub>O as the terminal ligands. Further inspection of the structural parameters reveals that **3** is a known complex, previously synthesized through the in situ reaction of Ni(OAc)<sub>2</sub>  $4H_2O$  and salicylhydrazide ligands [27]. This  $\{Ni_4\}$ complex is a rare example of a structure containing -N-N=N-N- bridges, which demonstrates the capacity of in situ reactions of this type to construct complexes with unusual structures.



Fig. 2 Supermolecular chain of 1 expanding along c-axis direction



**Fig. 3** Molecular structure of **2**. Selected geometric data: Fe(1)–N(1) 1.913(4); Fe(1)–N(3) 2.306(4); Fe(1)–N(4) 2.014(4); Fe(2)–N(5) 2.022(4); Fe(2)–N(6) 2.287(4); Fe(1)–O(1) 1.925(3); Fe(1)–O(2a) 1.929(4); Fe(2)–N(2) 1.916(4); Fe(2)–O(3) 1.918(4); Fe(2)–O(4b) 1.949(4) Å. N(1)–Fe(1)–O(1) 91.59(15); N(1)–Fe(1)–O(2a) 81.83(15);



Fig. 4 Molecular structure of 3. Ni(1)–N(1) 1.820(2); Ni(1)–N(4) 1.813(2); Ni(1)–O(1) 1.827(2); Ni(1)–O(4) 1.834(2); Ni(2)–O(6) 2.052(2); Ni(2)–N(2) 2.044(2); Ni(2)–N(3a) 2.041(2); Ni(2)–O(2) 2.0404(19); Ni(2)–O(3a) 2.0539(19); Ni(2)–O(5) 2.072(2) Å. N(1)–Ni(1)–O(1) 94.31(9); N(1)–Ni(1)–O(4) 176.79(9); N(4)–Ni(1)–O(1) 176.58(9); N(4)–Ni(1)–O(4) 94.43(9); N(4)–Ni(1)–N(1) 82.40(10); O(2)–Ni(2)–N(2) 77.19(8); O(2)–Ni(2)–N(3a) 174.78(8); N(2)–Ni(2)–O(3a) 174.57(8); N(2)–Ni(2)–O(5) 88.40(8); N(2)–Ni(2)–O(6) 96.01(9); N(3a)–Ni(2)–O(3a) 77.13(8); N(3a)–Ni(2)–O(5) 88.00(8); N(3a)–Ni(2)–O(6) 90.10(9); N(3a)–Ni(2)–N(2) 98.27(9)°. Symmetry codes: (a) –*x* – 2, –*y* + 1, –*z* – 1

A tentative mechanism can be suggested for the in situ generation of dshz anions in complexes 1 and 2 and aehba<sup>4–</sup> in 3. The H<sub>6</sub>mbshz contains four C–N bonds. As indicated by previous researchers, these acylhydrazine C–N bonds can undergo cleavage to generate formyl radicals under the catalysis of some transition metal salts [28, 29]. Given this observation, together with the structural analyses of 1–3, we speculate that four C–N bonds in H<sub>6</sub>mbshz

N(1)–Fe(1)–N(3) 105.76(16); N(1)–Fe(1)–N(4) 158.44(17); N(2)–Fe(2)–O(3) 91.63(15); N(2)–Fe(2)–O(4b) 81.26(15); N(2)–Fe(2)–N(5) 159.71(17); N(2)–Fe(2)–N(6) 106.58(16)°. Symmetry codes: (a) -x, -y, 1 - z; (b) 1 - x, 1 - y, 1 - z

are broken during the reactions, affording intermediates of salicylhydrazide, malonic dihydrazide, malonyl and phenoxyl free radicals. These free radicals further couple together in different combinations, along with coordination of the 3d metal ions, finally resulting in the formation of the complexes (Scheme 1). It is worth noting that these in situ reactions might include tandem C–N cleavages and C–N/N–N coupling processes, which has been rarely observed in previous studies. Furthermore, these observations provide insights that could be used to develop the syntheses of novel organic compounds.

#### Magnetic properties of the complexes

Variable-temperature magnetic susceptibility measurements for all three complexes were taken at a direct current field of 1000 Oe in the temperature range of 300-2 K. The  $\gamma_m T$  values of complexes 1 and 2 at room temperature are 0.72 and 11.81 cm<sup>3</sup> K mol<sup>-1</sup>, respectively, which are close to the expected values of 0.75 and 12  $\text{cm}^3$  K mol<sup>-1</sup> for non-interacting two Cu(II) ions (g = 2, S = 1/2) and four Fe(II) ions (g = 2, S = 2), respectively (Figs. 5, 6). The value for complex 3 (2.49  $\text{cm}^3 \text{ K mol}^{-1}$ ) is lower than the expected value for four magnetically isolated Ni(II) centers  $(4.84 \text{ cm}^3 \text{ K mol}^{-1}, g = 2.2, S = 1; \text{ Fig. 7}).$  Upon cooling, complexes 1-3 all show a steady decrease in  $\chi_{m-1}$ T values, reaching minima at 2 K of 0.20, 0.06 and  $0.05 \text{ cm}^3 \text{ K mol}^{-1}$ , respectively. Their magnetic susceptibilities all obey the Curie-Weiss law in the range of 100-300 K. The Curie constant C values are 0.75, 14.05 and 3.19 cm<sup>3</sup> K mol<sup>-1</sup> and Weiss constant  $\theta$  values are -11.72, -58.41 and -84.19 K, respectively (Figs. S4-S6).



Scheme 1 Possible in situ formation mechanism for ligands in 1-3



**Fig. 5**  $\chi_m T - T$  and  $\chi_m - T$  curves recorded under a 1000 Oe for **1**. The *red lines* represent the best fitting. (Color figure online)



**Fig. 6**  $\chi_m T - T$  and  $\chi_m - T$  curves recorded under a 1000 Oe for **2**. The *red lines* represent the best fitting. (Color figure online)

Both the profiles of  $\chi_m T - T$  curves and the negative  $\theta$  values suggest that antiferromagnetic interactions dominate between the metal ions in these complexes.



**Fig. 7**  $\chi_m T - T$  and  $\chi_m - T$  curves recorded under a 1000 Oe for **3**. The *red lines* represent the best fitting. *Inset* magnetic exchange pathways for **3** with a 2*J* model. (Color figure online)

To further explore their intramolecular magnetic interactions, the variable-temperature magnetic susceptibility data of complexes 1–3 were fitted using the Magpack Program [30, 31]. The fitting of 1 and 2 is based upon the Hamiltonian  $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$ . The magnetic interactions of 3 can be simplified as a Hamilton operator, as follows [32]:

$$\hat{H} = -2J_1\hat{S}_1 \cdot \hat{S}_2 - 2J_2 \left[ \sum_{i=1,2} \hat{S}_i \cdot \hat{S}_3 - \hat{S}_i \cdot \hat{S}_4 \right]$$

in which the terms  $J_1$  and  $J_2$  represent the magnetic interactions between Ni1 and Ni2 (or Ni2a), and Ni2 and Ni2a, respectively (Fig. 7 inset). The fitting results for all three complexes all agree well with their experimental data (Figs. 5, 6, 7). The best fit parameters are as follows: g = 2.1 and J = -23.2 cm<sup>-1</sup> for **1**, g = 2.0 and J = -4.3 cm<sup>-1</sup> for **2**, and g = 2.2,  $J_1 = -11.5$  cm<sup>-1</sup> and  $J_2 = -0.2$  cm<sup>-1</sup> for **3**. The strengths of these antiferromagnetic interactions are comparable to those of previously reported complexes with similar magnetic exchange pathways [33, 34].

# Conclusion

In conclusion, three complexes were obtained through coordination reactions between Cu, Fe and Ni salts and the diacylhydrazine ligand  $H_6$ mbshz. The in situ formations of bshz anions in **1** and **2** and aehba<sup>4-</sup> in **3** are thought to involve tandem C–N cleavage and C–N/N–N coupling processes via free radicals intermediates. All three complexes show dominant antiferromagnetic interactions. This work affords interesting and unusual examples of in situ ligand formation reactions and may provide insights that will prove to be of use in organic synthesis.

## Supplementary material

CCDC 1478797, 1478796 and 1503067 contain the supplementary crystallographic data for **1–3** in this paper. 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 33; or e-mail: deposit@ccdc.cam.ac.uk.

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