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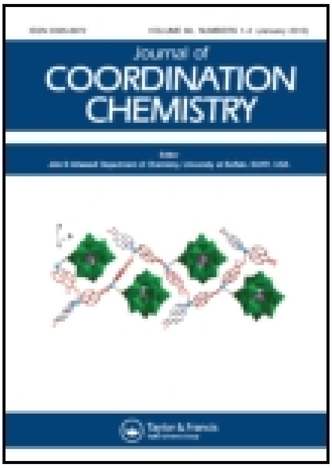

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One polynuclear copper(II) complex based on salicylaldehyde phenoxyacylhydrazone: structural and magnetic studies

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One polynuclear copper(II) complex based on salicylaldehyde phenoxyacylhydrazone: structural and magnetic studies

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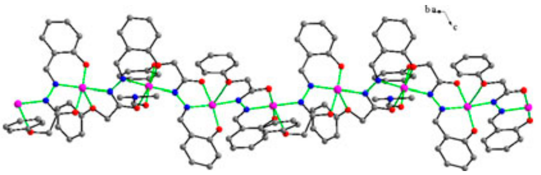

One new copper(II) complex with a multidentate Schiff-base ligand salicylaldehyde phenoxyacylhydrazone (H_2L), $\{[Cu_4(L)_4(DMF)]\cdot DMF\}_n$ (**1**) has been synthesized and structurally characterized. Complex **1** exhibits a coordination polymer with a 1-D infinite chain-like structure, resulting from the Cu(II) centers linked by N–N single bonds. Magnetic behavior of **1** shows that it is antiferromagnetic.

Keywords: Polynuclear copper(II) complex; Crystal structure; Magnetic properties

1. Introduction

The synthesis of polynuclear complexes and coordination polymers attracts attention for their intriguing structural motifs and potential applications in magnetochemistry, bioinorganic chemistry, materials chemistry, and solid-state chemistry [1–7]. Many factors affect the formation of polynuclear complexes and coordination polymers with selection of the organic ligands being one of the most important factors [8–11]. Many types of ligands such as alkoxides [12], oximates [13], and carboxylates [14] have been used for the synthesis of such complexes. *N*-Salicylaldehyde acylhydrazone ligands derived from the condensation of salicylaldehyde with an acylhydrazide, as a type of multidentate ligand with potential O- or N-donors, have been used in the construction of a series of polynuclear complexes and coordination polymers incorporating Cu(II), Ni(II), and Mn(III) ions [15–18]. *N*-Salicylaldehyde acylhydrazone ligands containing phenoxy groups, derived from the condensation of

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*Corresponding author. Email: xiaohuachen03@163.com salicylaldehyde with phenoxy carboxylic acid hydrazide {Ph–O–C(O)–NH–NH_2} or its derivatives, though little explored, show interesting functional properties due to flexible coordination modes, and a few transition metal complexes have been reported. Most are mononuclear complexes with discrete structures [19–25], except three examples of copper compounds $[Cu(L1)(C_5H_5\ N)]_2 \cdot 2CH_3OH$ and $[Cu(L1)(C_4H_9NO)]_n$ (H_2L1 = 2-(2-chlorophenoxy)-N′-(2-hydroxybenzylidene)-acetohydrazide) [26, 27], and $\{[Cu(L2)] \cdot DMF \cdot H_2O\}_n$ (H_2L2 = 2-(naphthalene-2-yloxy)-N′-(2-hydroxybenzylidene)acetohydrazide) [28]. The first mentioned complex forms a dinuclear structure and the last two examples were one-dimensional (1-D) chain structures. Based on this background, and in continuation of our previous work on polynuclear complexes and coordination polymers with these kinds of hydrazone ligands containing phenoxy groups, we report the synthesis, structure, and magnetic properties of one new copper(II) complex derived from a bridging multidentate ligand H_2L (salicylaldehyde phenoxyacylhydrazone), $\{[Cu_4(L)_4(DMF)] \cdot DMF\}_n$ (**1**). Complex **1** is generated into a 1-D chain-like complex polymer with N–N groups as bridges. To the best of our knowledge, complex **1** is the rare example of 1-D chain-like copper–hydrazone compounds constructed by diazine N–N bridges [18, 28].

2. Experimental

2.1. *Material and instrumentation*

All organic solvents and materials used for synthesis were of reagent grade and used without purification. The Schiff base H_2L was prepared following the published procedure [20]. Elemental analyses for C, H, and N were carried out with an Elementar Vario EL III microanalyser. IR spectra were recorded on a Perkin-Elmer spectrum 2000 spectrophotometer with KBr pellets from 4000 to 400 cm^{-1}. Thermal analyses were performed on a TGA-SDTA 851^e thermogravimetric analyzer with a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. ESR spectra were recorded at room temperature at X-band frequency with a Bruker EMX 10/12 automatic spectrometer. Temperature-dependent magnetic susceptibility measurements were carried out on a powdered sample of the complex using a Quantum Design MPMS-7XL SQUID magnetometer.

2.2. *Synthesis of 1*

A methanol solution (5 mL) of H_2L (0.1 mM) was added to a DMF (5 mL) solution of $CuCl_2 \cdot H_2O$ (0.1 mM), and the mixture was stirred at room temperature for 2 h. The dark green solution was filtered and allowed to stand at room temperature for a few days. Green crystals of **1** suitable for structural analysis were obtained with a 36% yield based on Cu. Anal. Calcd for $C_{66}H_{62}Cu_4N_{10}O_{14}$: C, 53.80; H, 4.24; N, 9.51. Found: C, 53.88; H, 4.12; N, 9.65. IR (KBr, cm^{-1}): 3072 (m, br), 1600 (s), 1527 (s), 1487 (w), 1444 (m), 1364 (s), 1337 (w), 1258 (w), 1134 (s), 1029 (w), 892 (s), 768(m), 693 (s), 620 (m).

2.3. *Structure determination*

A crystal of **1** with suitable size was selected for the structure analysis. Intensity data were collected on a Rigaku RAPID Weissengberg IP diffractometer with graphite-monochromated

Mo Kα radiation (λ = 0.71073 Å) and the ω scan mode. The structure was solved by direct methods with SHELXS-97 [29] and refined by full matrix least squares calculations with SHELXL-97 [30]. The carbon C62 of DMF in **1** is disordered and has been modeled over two sites with equal occupancies of 0.5. The C62 and C63 of DMF in **1** were refined isotropically. All the other non-hydrogen atoms in the two compounds were refined anisotropically. The hydrogens attached to C62 in **1** were not located. All the other hydrogens were found from difference Fourier syntheses and geometrical calculation. Crystallographic data for **1** are listed in table 1.

3. Results and discussion

3.1. *Crystal structure of 1*

Selected bond lengths and angles for **1** are given in table 2. Single-crystal X-ray analyses revealed that the main fragment of **1** is a tetranuclear $[Cu_4(L)_4(DMF)]$ unit. The tetranuclear unit consists of four pentadentate L^{2-} ligands bound to four copper centers in an approximately linear array, with all ligand donor sites involved in coordination. The four copper ions are directly linked by three almost *trans* diazine N–N bridges. Simultaneously, neighboring tetranuclear subunits are connected by a single N–N bridge, resulting in a 1-D polymer with $[–Cu–N–N–]_4$ cores as shown in figure 1. A packing view along the *b* direction is depicted in figure 2. The N–N bond distances are 1.398(3)–1.406(3) Å, indicative of N–N

Table 1. Crystallographic data for **1**.

Empirical formula	$C_{66}H_{62}Cu_4N_{10}O_{14}$
Formula weight	1473.42
Crystal size (mm^3)	0.42 × 0.21 × 0.10
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	14.1900(12)
b (Å)	15.2738(11)
c (Å)	17.2037(12)
α (°)	108.163(3)
β (°)	104.879(3)
γ (°)	103.244(4)
Volume (Å^3), *Z*	3224.2(4), 2
Temperature (K)	293
Calculated density (g cm^{-3})	1.518
Absorption coefficient (mm^{-1})	1.375
F (0 0 0)	1512
θ Range for data collection (°)	1.49–26.00
Index range *h*	−17 → 16
k	0 → 18
l	−21 → 20
No. of independent reflections	12,276
No. of observed reflections [$I > 2\sigma(I)$]	9133
Parameters	845
Restraints	2
Goodness of fit on F^2	1.071
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0422, 0.1101
Final R_1, wR_2 (all data)	0.0620, 0.1189
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.624, −0.557

Note: $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(|F_o^2 - F_c^2|)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

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

Cu(1)–O(4)	1.896(2)	Cu(1)–N(3)	1.929(2)
Cu(1)–O(5)	1.965(2)	Cu(1)–N(2)	1.984(2)
Cu(1)–O(3)	2.588(2)	Cu(2)–O(7)	1.897(2)
Cu(2)–N(5)	1.938(2)	Cu(2)–O(8)	1.976(2)
Cu(2)–N(4)	2.000(2)	Cu(2)–O(6)	2.561(2)
Cu(2)–O(13)	2.494(4)	Cu(3)–O(10)	1.882(2)
Cu(3)–N(7)	1.928(2)	Cu(3)–O(11)	1.989(2)
Cu(3)–N(6)	1.990(2)	Cu(3)–O(9)	2.409(3)
Cu(4)–O(1A)	1.881(3)	Cu(4)–N(1A)	1.921(2)
Cu(4)–O(2A)	1.945(2)	Cu(4)–N(8)	1.989(2)
Cu(4)–O(12)	2.533(2)	O(2)–C(8)	1.284(3)
N(1)–N(2)	1.406(3)	N(2)–C(8)	1.321(4)
N(1)–C(7)	1.283(4)	O(5)–C(23)	1.268(3)
N(3)–N(4)	1.404(3)	N(4)–C(23)	1.317(4)
N(3)–C(22)	1.283(4)	O(8)–C(38)	1.274(4)
N(5)–N(6)	1.398(3)	N(6)–C(38)	1.319(4)
N(5)–C(37)	1.290(4)	O(11)–C(53)	1.269(4)
N(7)–N(8)	1.398(3)	N(8)–C(53)	1.301(4)
N(7)–C(52)	1.293(4)	Cu(1)···Cu(2)	4.7667(6)
Cu(2)···Cu(3)	4.7585(6)	Cu(3)···Cu(4)	4.7377(6)
Cu(4)···Cu(1A)	4.7231(6)		
O(4)–Cu(1)–N(3)	92.78(10)	O(4)–Cu(1)–O(5)	169.93(10)
N(3)–Cu(1)–O(5)	81.28(9)	O(4)–Cu(1)–N(2)	91.29(10)
N(3)–Cu(1)–N(2)	175.09(10)	O(5)–Cu(1)–N(2)	95.07(9)
O(3)–Cu(1)–O(4)	103.5(1)	O(3)–Cu(1)–O(5)	85.88(9)
O(3)–Cu(1)–N(2)	71.94(9)	O(3)–Cu(1)–N(3)	104.39(9)
O(7)–Cu(2)–N(5)	93.37(10)	O(7)–Cu(2)–O(8)	174.44(9)
N(5)–Cu(2)–O(8)	81.11(9)	O(7)–Cu(2)–N(4)	90.57(10)
N(5)–Cu(2)–N(4)	166.44(11)	O(8)–Cu(2)–N(4)	94.97(10)
O(6)–Cu(2)–O(7)	84.07(11)	O(6)–Cu(2)–O(8)	96.97(11)
O(6)–Cu(2)–N(4)	73.49(9)	O(6)–Cu(2)–N(5)	94.01(9)
O(13)–Cu(2)–O(7)	90.57(13)	O(13)–Cu(2)–O(8)	88.55(13)
O(13)–Cu(2)–N(4)	104.70(11)	O(13)–Cu(2)–N(5)	88.24(12)
O(6)–Cu(2)–O(13)	174.3(1)	O(10)–Cu(3)–N(7)	92.89(10)
O(10)–Cu(3)–O(11)	172.34(10)	N(7)–Cu(3)–O(11)	80.49(9)
O(10)–Cu(3)–N(6)	91.64(10)	N(7)–Cu(3)–N(6)	171.19(11)
O(11)–Cu(3)–N(6)	95.45(10)	O(10)–Cu(3)–O(9)	96.11(10)
N(7)–Cu(3)–O(9)	114.25(10)	O(11)–Cu(3)–O(9)	83.25(10)
N(6)–Cu(3)–O(9)	72.73(10)	O(1A)–Cu(4)–N(1A)	94.11(11)
O(1A)–Cu(4)–O(2A)	170.06(11)	N(1A)–Cu(4)–O(2A)	81.46(9)
O(1A)–Cu(4)–N(8)	92.04(11)	N(1A)–Cu(4)–N(8)	172.36(11)
O(2A)–Cu(4)–N(8)	93.13(10)	O(12)–Cu(4)–O(1A)	74.16(5)
O(12)–Cu(4)–O(2A)	74.12(5)	O(12)–Cu(4)–N(1A)	73.62(5)
O(12)–Cu(4)–N(8)	74.41(9)		

Note: Symmetry codes: A: $x + 1$, $y + 1$, $-z$.

single bonds. The separations of the copper–copper ions exceed 4.7 Å (Cu(1)···Cu(2) 4.7667(6) Å, Cu(2)···Cu(3) 4.7585(6) Å, Cu(3)···Cu(4) 4.7377(6) Å, Cu(4)···Cu(1A) 4.7231(6) Å). The torsion angles of Cu(1)–N(3)–N(4)–Cu(2), Cu(2)–N(5)–N(6)–Cu(3), Cu (3)–N(7)–N(8)–Cu(4), and Cu(4)–N(1A)–N(2A)–Cu(1A) are 169.66(14)°, 172.47(14)°, 168.26(14)°, and 169.02(12)°, respectively. These data are similar to the corresponding ones found in the copper–hydrazone complexes $\{[Cu(L2)]\cdot DMF\cdot H_2O\}_n$ [28] and $[Cu_2(C_{14}H_{11}N_3O_3)(acac)(H_2O)]ClO_4$ [31], in which the neighboring Cu(II) ions are also connected by single N–N bonds.

The four copper ions have two kinds of coordination environments, distorted square-pyramidal and octahedral. The distortion indexes τ [32] for Cu(1), Cu(3), and Cu(4) are

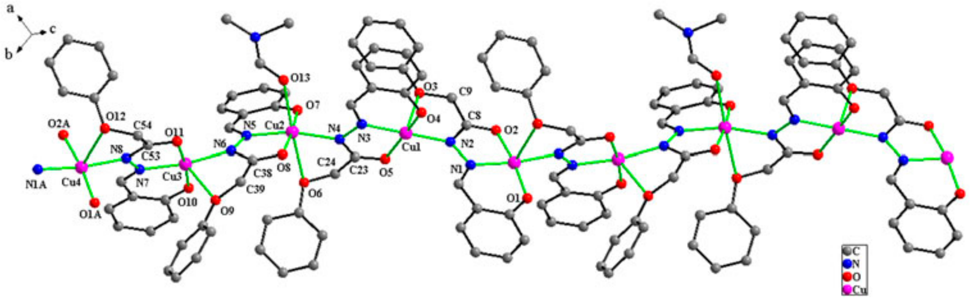

Figure 1. The 1-D chain structure of **1** [symmetry code: (A) $x + 1, y + 1, z$].

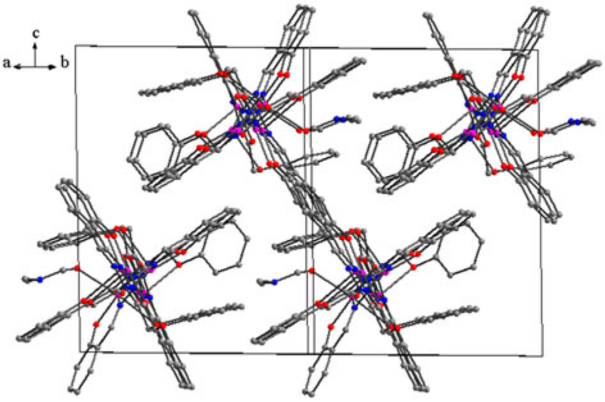

Figure 2. Packing diagram of **1** along the *b*-axis.

0.09, 0.02, and 0.04, respectively ($\tau = 0$ and 1 for ideal square pyramid and trigonal bipyramid, respectively), indicating distorted square pyramidal geometries around the three copper ions. Each basal plane of the square-pyramids is defined by one phenolic oxygen, one amide oxygen, and one azomethine nitrogen from the first L^{2-} ligand, and one amide nitrogen of the second L^{2-}, while the axial site is occupied by the ether of the phenoxy group from the second L^{2-} ligand. The Cu–O_{basal} and Cu–N_{basal} bond lengths are comparable with the bond lengths reported for copper complexes with the same coordinating atoms [18, 28]. Owing to the Jahn–Teller effect, the axial Cu–O(ether) bond distances (2.409(3)–2.588(2) Å) for these Cu(II) ions are much longer than those in the basal positions (table 2). Long, and presumably weak, bonding interactions between Cu(II) and ether oxygen have also been encountered in the copper–hydrazone complex $\{[Cu(L2)]\cdot DMF\cdot H_2O\}_n$ [28], in which the corresponding distance is 2.501(2) Å. However, in the other reported metal–hydrazone complexes containing phenoxy groups, these potential donors have not been found to coordinate [19–27]. In **1**, Cu(2) adopts a distorted octahedral CuN_2O_4 coordination geometry with typical Jahn–Teller effect for Cu(II). The equatorial position of Cu(2) is also occupied by one phenolic O, one amide O, and one azomethine N from the first L^{2-} ligand, and one amide nitrogen of the second L^{2-}. The axial positions of Cu(2) are occupied by one ether O of the second L^{2-} ligand and one oxygen of DMF. The axial bond lengths of Cu(2)–O(6) and Cu(2)–O(13) are 2.561(2) and 2.494(4), respectively, indicating that O(6) and O(13) are weakly coordinated to Cu(2).

Two mononuclear coordination compounds derived from the same ligand salicylaldehyde phenoxyacylhydrazone have been reported [20, 21], in which the L^{2-} has normal tridentate coordination modes. However, each L^{2-} in **1** has tridentate coordination to one Cu(II) and simultaneously bidentate coordination to a neighboring Cu(II). Three of the four ligands within the $[Cu_4(L)_4(DMF)]$ unit are distorted from the planar conformation, confirmed by the dihedral angle between the two phenyl rings in each L^{2-} [41.0(2), 68.6(2), and 79.6(2)°, respectively], but the remaining ligand containing O(1) is nearly planar with a mean deviation from the least square plane of 0.0653(3) Å. The difference may be attributed to the conformational flexibility for the benzenyloxyacetate groups. The N–N, N=C, and C–O bond lengths in the $–C{=}N–N{=}C(O^{-})–$ fragments of L^{2-} are consistent with the enolate form of the hydrazone functionalities [28, 33].

3.2. *Thermal analysis of 1*

The thermal properties of **1** were characterized by thermogravimetric analysis under nitrogen from 30 to 800 °C (figure S1, see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.951344). For **1**, a weight loss of 35.7% from 240 to 320 °C observed in the TG curve can be ascribed to the loss of two DMF molecules and four C_6H_5O groups (Calcd 35.2%). Then, gradual weight loss from 380 to 530 °C temperature can be assigned to decomposition of the organic ligands. The mass remnant of 20.9% at 500 °C corresponds to deposition of CuO (Calcd value 21.6%).

3.3. *ESR spectra of 1*

The X-band polycrystalline ESR spectra of **1** are plotted in figure 3. At both room temperature and 110 K, the complex exhibits only a symmetrical signal centered at about g = 2.09. Such a featureless ESR signal may be due to the relatively strong antiferromagnetic interaction between neighboring copper(II) ions.

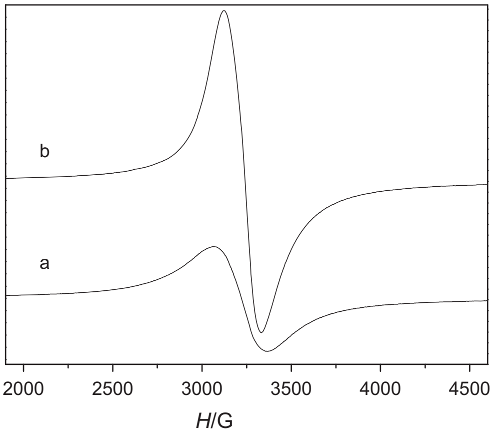

Figure 3. X-band ESR spectra of **1** at room temperature (a) and 110 K (b).

3.4. *Magnetic study of 1*

The magnetic susceptibility of **1** was measured from 2 to 300 K and shown as $\chi_M T$ and χ_M *versus* T plots in figure 4. The $\chi_M T$ value per Cu(II) ion at room temperature is 0.29 emu M^{-1} K, significantly lower than the spin-only value for S = 1/2, suggesting antiferromagnetic interactions between neighboring Cu(II) ions. Upon cooling, the χ_M value first increases and then decreases in the 300–11 K temperature range, giving a broad maximum centered at ca. 135 K. The $\chi_M T$ product decreases monotonically with decreasing temperature, consistent with the antiferromagnetic interactions [34]. Upon cooling further below 11 K, the χ_M value exhibits a rapid increase, and the $\chi_M T$ product tends to reach a plateau. Such low-temperature behaviors are attributable to the presence of paramagnetic impurity.

According to the structural data of **1**, there are two possible exchange pathways between neighboring Cu(II) ions: the N–N diazine bridge and the O–C–C–O linkage. The latter may be neglected for the following reasons: (i) the latter is longer and contains a sp^3 carbon, through which the spin communication is smaller than that through the shorter N–N linkage; (ii) for Cu(II) with an axially elongated square-pyramidal or octahedral geometry, the magnetic orbital is of d(x^2-y^2) type and delocalization of the spin density towards the axial atom is poor. In **1**, the phenoxy oxygen in the O–C–C–O linkage occupies the axial position, so the magnetic exchange via this pathway is expected to be very small. In contrast, both nitrogens in the diazine bridge are located in equatorial positions, and the magnetic interaction through such a bridge should be much more efficient. Based on the chain structure, four J parameters are needed to account for the intrachain magnetic interactions for different pairs of neighboring Cu(II) ions.

$$-\mathrm{Cu}_1\overset{J_1}{-}\mathrm{Cu}_2\overset{J_2}{-}\mathrm{Cu}_3\overset{J_3}{-}\mathrm{Cu}_4\overset{J_4}{-}\mathrm{Cu}_1-\mathrm{Cu}_2-\mathrm{Cu}_3-\mathrm{Cu}_4-$$

No analytical expression of magnetic susceptibility for this four-J system has been developed. In **1**, although the Cu(II) ions differ from one another, the differences mainly lie in the axial coordination, which is expected to impose little influence upon magnetic communications, as suggested above. The equatorial coordination parameters of the four Cu(II) ions exhibit no significant differences, and more importantly, the Cu–N–N–Cu torsion angles are very similar. One may suggest that the interactions mediated by the four diazine bridges be very similar. It follows that the magnetic behavior of the chain may be accounted for by a simple one-J model. We applied the theoretical expression proposed by Hall for antiferromagnetic uniform chains with local spin S = 1/2:

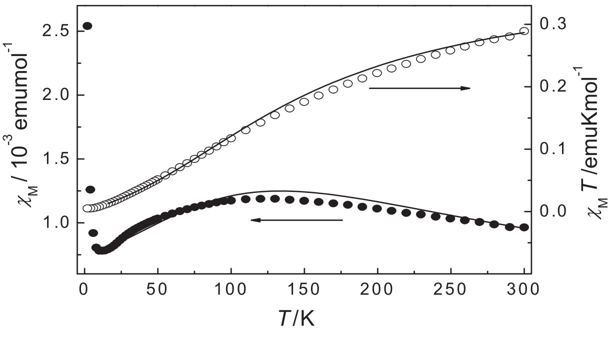

Figure 4. Plots of $\chi_M T$ (○) *vs.* T and χ_M (●) *vs.* T for **1**. The theoretical fit to experimental data is shown by solid line.

$$\chi_M = \frac{N\beta^2 g^2}{kT}\frac{0.25 + 0.14995x + 0.30094x^2}{1 + 1.9862x + 0.68854x^2 + 6.0626x^3}$$

where $x = |J|/kT$. The best fit of the expression to experimental data above 15 K yields $J = -125\ \text{cm}^{-1}$ and $g = 2.0$. The large negative J value indicates that the strong antiferromagnetic interactions are transmitted between Cu spins via the diazine N–N linkage. The magnitude of the magnetic exchange coupling constant is comparable to that ($J = -134\ \text{cm}^{-1}$) reported in the copper complex $\{[Cu_3(po2p\text{-}H)_2(H_2O)_2](ClO_4)_4\cdot 2H_2O\}$ [35] with the neighboring copper centers connected just by N–N single bonds from the hydrazone ligands. Similar with **1**, the copper centers in $\{[Cu_3(po2p\text{-}H)_2(H_2O)_2](ClO_4)_4\cdot 2H_2O\}$ are in an almost fully *trans* arrangement around the N–N bonds with the Cu–N–N–Cu torsional angles being 169.0° and 176.3°. The substantially larger exchange integral in **1** and $\{[Cu_3(po2p\text{-}H)_2(H_2O)_2](ClO_4)_4\cdot 2H_2O\}$ is entirely consistent with their conformational feature.

4. Conclusion

A copper complex $\{[Cu_4(L)_4(DMF)]\cdot DMF\}_n$ with multidentate salicylaldehyde phenoxyacylhydrazone ligand (H_2L) is characterized by crystal structure analysis and variable temperature magnetic susceptibility measurement. In contrast with the reported discrete mononuclear structures with the same ligand, the unusual characteristic of **1** is a 1-D chain-like complex polymer, which was self-assembled by N–N single bond bridges as the main intrametallic and intermetallic connection. Magnetic measurements of **1** revealed the presence of antiferromagnetic coupling interaction between adjacent copper centers, in complete agreement with previous studies.

Supplementary material

Crystallographic data has been deposited with the Cambridge Crystallographic Center with CCDC No. 9976640. Supplementary data is available from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: t441223336033; E-mail: deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk) on request.

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