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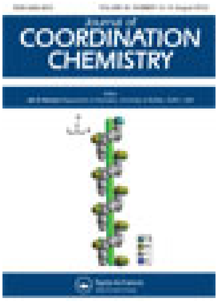

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Synthesis and structure of amide oxygen-bridged polymeric and monomeric copper(II) complexes with aroylhydrazones

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The synthesis and structure of two Cu(II) complexes, $\{[Cu_2(L^1)_2]\cdot DMF\}_n$ (**1**) and $[CuL^2(phen)]$ (**2**), are described. The dinegative hydrazones are obtained by deprotonation of both phenolic and amide moieties of *N*′-(5-bromo-2-hydroxybenzylidene)-3,5-dimethoxybenzohydrazide (H_2L^1) and *N*′-(2-hydroxybenzylidene)pyrazine-2-carbohydrazide (H_2L^2). In each complex the planar ligand binds the metal ion *via* phenolate-O, imine-N, and amide-O. Complex **1** is a polymer in which phenoxo-bridged binuclear Cu(II) units are further joined by equatorial–apical amide-O bridges. The Cu⋯Cu separations are 3.0306 and 3.8217 Å for the phenolate-O bridged pair and the amide-O bridged pair, respectively. Complex **2** is a monomer where chelating phen displays axial–equatorial bonding, with square-pyramidal Cu(II).

Keywords: Polymeric chain; Amide oxygen bridge; Phenolate oxygen bridge; Cu(II) hydrazone complex; Crystal structure

1. Introduction

Current efforts have been devoted to self-assembly of molecular building blocks containing organic ligand and transition metal ions, which provides a reliable and efficient approach for design and construction of metal–organic frameworks [1–3]. Aroylhydrazones are a class of versatile ligands capable of forming different molecular architectures. The coordination chemistry of aroylhydrazones as well as the molecular structure of a number of Cu(II) complexes has been studied [4–19].

Square-planar Cu(II) complexes with *N*-salicylideneacylhydrazines are known to form dimeric species containing equatorial–apical bridges due to involvement of the metal ion in weak interactions with neighboring molecules at the apical position [13, 16]. However, the identity of the bridging atom is ambiguous [17]. The X-ray molecular structures reported for all dimeric copper(II) complexes with *N*-salicylideneacylhydrazines with different degrees of deprotonation indicate dimerization through the phenoxy oxygen [8–18]. However, amide oxygen-bridged dinuclear complexes are particularly attractive for the study of the influence of amide proton on the interaction

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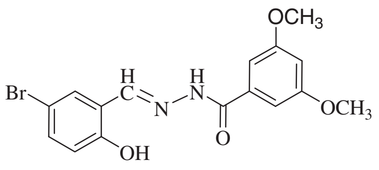
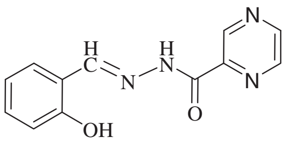
between metal ions [17]. Although the amide oxygen-bridged structure is proposed based on IR and magnetic study [18, 20], the actual structure of this type of dimeric complex remains in doubt until an X-ray molecular structure is available. To the best of our knowledge, only one structure of a dimeric Cu(II) complex with amide oxygen participating in equatorial–apical bridging is reported [10].

Continuing our work [21–25] on the coordination chemistry of substituted aroylhydrazones with heterocycles to examine the possible change in coordination of the ligands and its concomitant effect on the solid state supramolecular assembly, we report here the syntheses and structures of polymeric $\{[Cu_2(L^1)_2]\cdot DMF\}_n$ (**1**) and monomeric $[CuL^2(phen)]$ (**2**) with aroylhydrazones. Complex **1** constitutes an example of polymeric Cu(II) complex of aroylhydrazones *via* equatorial–apical amide-O bridges employing phenoxo-bridged binuclear Cu(II) units as building blocks. The present polymeric chain is further stabilized by intermolecular hydrogen bonds, giving a 2-D network. In **2**, the bidentate phen saturates the square-pyramidal arrangement around Cu(II) and precludes the dimerization observed in other Cu(II) complexes of aroylhydrazones.



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. Cyclic voltammetry measurements were performed on an LK98 Microcomputer-based electrochemical analyzer with a glassy carbon working electrode, a platinum wire counter electrode, and Ag–AgCl as reference electrode. Tetrabutylammonium hexafluorophosphate (TBAHFP) ($0.1\,mol\,dm^{-3}$) was the supporting electrolyte. The substituted aroylhydrazones, H_2L^1 and H_2L^2, were prepared by condensation of 3,5-dimethoxybenzohydrazine and pyrazine-2-carbohydrazide with 5-bromo-salicylaldehyde and 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. $\{[Cu_2(L^1)_2]\cdot DMF\}_n$ (1). To a mixed solution of methanol ($10\,cm^3$) and DMF ($5\,cm^3$) of H_2L^1 (0.076 g, 0.2 mmol) and pyrazine (0.048 g, 0.6 mmol), a methanol solution (10 cm^3) of $Cu(O_2CCH_3)_2 \cdot H_2O$ (0.038 g, 0.2 mmol) was added gradually with stirring. The resulting green solution was further stirred for 2 h and filtered. Greenish brown crystals after about one week were collected. Yield: 60%; m.p. > 300°C. Anal. Calcd for **1** (%): C, 44.04; N, 7.34; H, 3.48. Found: C, 44.14; N, 7.42; H, 3.56.

2.2.2. [CuL^2(phen)] (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 phen (1 : 1 : 3 mole ratio) in a mixed solution of methanol and DMF; m.p. > 300°C. Anal. Calcd for **2** (%): C, 59.56; N, 17.36; H, 3.33. Found: C, 59.64; N, 17.46; H, 3.45.

2.3. *Crystal structure determinations*

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) and 223(2) K, respectively. 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 hydrogen atoms were located geometrically and refined isotropically. For **1**, C17, C18, C19, and O_5 of DMF were disordered over two positions, with site occupation factors of 0.50/0.50. 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	$C_{35}H_{33}Br_2Cu_2N_5O_9$	$C_{24}H_{16}CuN_6O_2$
Formula weight	954.56	483.97
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/*n*	P2(1)/*n*
Unit cell dimensions (Å, °)		
a	15.4689(15)	10.111(2)
b	5.9120(8)	11.671(2)
c	19.4546(19)	17.735(4)
α	90	90
β	94.4930(10)	98.04(3)
γ	90	90
Volume (Å^3), Z	1773.7(3), 2	2072.2(7), 4
Calculated density (g cm^{-3})	1.787	1.551
Absorption coefficient (mm^{-1})	3.515	1.090
$F(000)$	956	988
Max. and min. transmission	0.7663/0.5399	0.8535/0.6117
θ range for data collection (°)	2.64–25.02	3.35–26.00
Reflection collected	8429	10,387
Independent reflection	3112 [R(int) = 0.1254]	4014 [R(int = 0.0664]
Reflections with [$I > 2\sigma(I)$]	2160	2632
Data/restraints/parameters	3112/0/259	4014/0/298
Goodness-of-fit on F^2	1.056	0.988
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0615$, $wR_2 = 0.1564$	$R_1 = 0.0697$, $wR_2 = 0.1660$
R indices (all data)	$R_1 = 0.0850$, $wR_2 = 0.1794$	$R_1 = 0.1017$, $wR_2 = 0.1852$

3. Results and discussion

3.1. *Synthesis*

The two complexes have been synthesized by adding the metal ion solution to solution of a mixture of H_2L and excess amount of heterocycle to prevent the precipitation of the insoluble dimeric species commonly obtained with similar tridentate dinegative ligands [10, 17–19]. However, in **1**, heterocycle pyrazine does not participate in the coordination.

3.2. *IR spectra and electronic spectra*

IR spectra of the two complexes do not display a band assignable to C = O of the amide in the tridentate Schiff base at *ca* 1650 cm^{-1}, consistent with deprotonation and the enolate form of the amide [11, 12]. A strong band attributed to conjugated C=N–N=C is observed at 1592 cm^{-1} for **1** and 1604 cm^{-1} for **2** [22–24].

The electronic spectrum of **1** shows bands at 270, 305, 327, 369, and 411 nm. The electronic spectrum of **2** shows bands at 272, 304, 315, 333, and 394 nm. The absorption peaks between 270 and 369 nm can be assigned to intraligand transition, and the absorption band at *ca* 400 nm may correspond to the ligand-to-metal charge transfer [22–24].

3.3. *Cyclic voltammetry*

Cyclic voltammograms of **1** and **2** were measured in DMF containing 0.1 mol L^{-1} TBAHFP. Complex **1** exhibits two irreversible cathodic waves at −0.719 and −1.031 V (*vs.* Ag/AgCl), which can be attributed to reductions at the metal center, Cu(II)Cu(II) → Cu(II)Cu(I) and Cu(II)Cu(I) → Cu(I)Cu(I), respectively [26, 27]. Complex **2** shows an irreversible cathodic wave at −0.617 V (*vs.* Ag/AgCl), assigned to Cu(II) to Cu(I) reduction. Similar results have previously been reported for Cu(II) complexes with Schiff-base ligands [21, 28, 29].

3.4. *Crystal structure of 1*

The structure of **1** consists of polymeric $[Cu_2(L^1)_2]$ linked by equatorial–apical amide-O bridges. The crystallographically independent phenolate-O bridged dinuclear $[Cu_2(L^1)_2]$ unit is shown in figure 1 with the atom-numbering scheme. A view of a segment of the chain growing through a screw axis parallel to *b* is depicted in figure 2. Selected bond lengths and angles for **1** are listed in table 2.

In the phenolate-O bridged dinuclear $[Cu_2(L^1)_2]$ unit, each Cu(II) is coordinated to phenolate-O, the imine-N and the deprotonated amide-O of the dinegative tridentate ligand. The fourth coordination site is occupied by the symmetry-related phenoxy oxygen of the other monomeric unit. In this Cu_2O_2 core, each Cu(II) lies approximately in the ligand plane showing a slight deviation of 0.031 Å. The Cu1···Cu1A separation (3.0306(16) Å) and the Cu1–O4–Cu1A bridge angle (101.01(19)°) are comparable to those observed in other phenoxo-bridged dimeric Cu(II) complexes with tridentate aroylhydrazones [14–19].

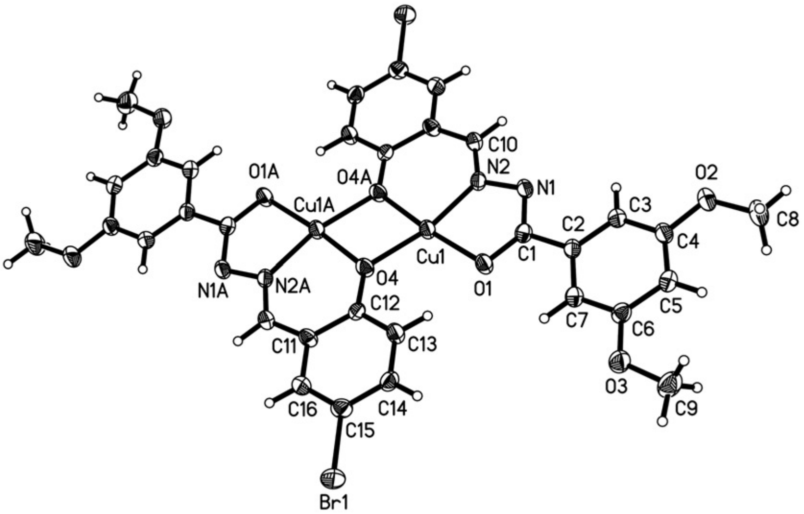


Figure 1. Structure of $\{[Cu_2(L^1)_2]\cdot DMF\}_n$ (**1**) with the atom-numbering scheme. Disordered DMF is omitted for clarity.

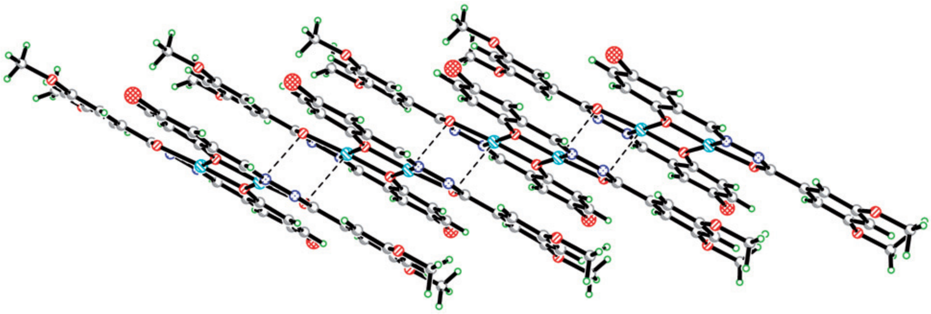


Figure 2. Amide oxygen-bridged polymeric chain of $\{[Cu_2(L^1)_2]\cdot DMF\}_n$ (**1**).

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

Cu(1)–N(2)	1.900(5)	Cu(1)–O(1)	1.959(5)
Cu(1)–O(4)	1.967(4)	Cu(1)–O(4)A#1	1.960(4)
Cu(1)–Cu(1)A#1	3.0306(16)		
N(2)–Cu(1)–O(1)	81.6(2)	N(2)–Cu(1)–O(4)A#1	92.7(2)
N(2)–Cu(1)–O(4)	167.7(2)	O(1)–Cu(1)–O(4)	106.92(18)
O(1)–Cu(1)–O(4)A#1	173.95(18)	O(4)A#1–Cu(1)–O(4)	78.99(19)
Cu(1)A#1–O(4)–Cu(1)	101.01(19)		

Symmetry transformations used to generate equivalent atoms: #1: $-x+1$, $-y$, $-z+1$.

The dinuclear $[Cu_2(L^1)_2]$ unit does not coordinate to solvent to complete the well-known square pyramid around Cu(II) observed in other phenoxo-bridged dimeric copper(II) complexes [14–19]. Adjacent dinuclear $[Cu_2(L^1)_2]$ units are linked through axial amide-O bridges into a linear stepped polymer with each Cu(II) displaying a distorted square pyramid (figure 2). In this Cu_2O_2 core, the Cu1–O1# ($-x+1$,$-y$, $-z+1$) and the Cu1$\cdots$Cu2 distances are 2.8725(6) and 3.8217(2) Å, respectively.

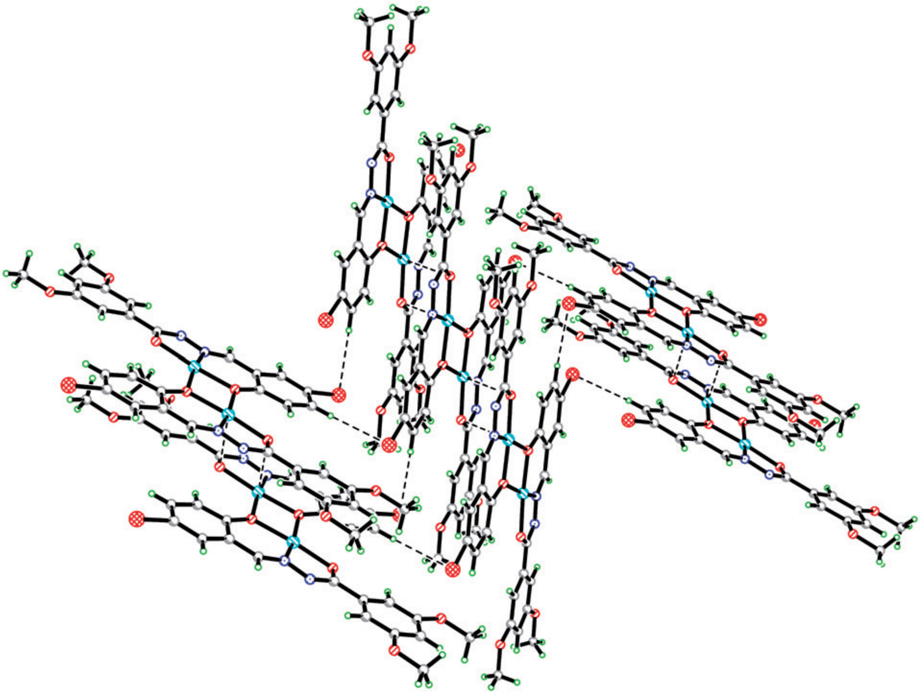


Figure 3. 2-D arrangement of $\{[Cu_2(L^1)_2] \cdot DMF\}_n$ (**1**) in the crystal lattice. Disordered DMFs are omitted for clarity.

The Cu1–O1–Cu2 bridge angle is 102.930(5)°. Cu–O(phenolate) (1.967(4) Å) and Cu–O(amide) (1.959(5) Å) distances are significantly longer than the only reported equatorial–apical amide-O bridged dimeric Cu(II) complex $[Cu(bhs)(Hpyrz)] \cdot 0.5H_2O$ (1.865(3) and 1.929(3) Å) [10], apparently due to the polymerization of **1** *via* equatorial–apical amide-O employing the phenoxo-bridged binuclear Cu(II) units as building blocks. The Cu–N(imine) (1.900(5) Å) distance is comparable to that observed in $[Cu(bhs)(Hpyrz)] \cdot 0.5H_2O$ (1.902(3) Å) [10].

The polymers are interconnected through weak hydrogen bonds between C–H and bromide with C···Br distance of 3.953 Å, resulting in a 2-D network (figure 3).

3.5. *Crystal structure of 2*

The molecular structure of **2** with the atom-numbering scheme is illustrated in figure 4, and selected bond parameters are listed in table 3.

Cu(II) is a distorted square pyramid with basal coordination positions occupied by phenolate O1, imine N4, and the deprotonated amide O2 of the dinegative tridentate ligand, and N6 of phen. The apical position is occupied by N5 of phen.

The ligand forms an O_2N_2 square plane around Cu(II) with the largest deviation from the mean plane of 0.0355 Å for N4 and copper displaced by 0.1541 Å from the basal plane toward the apical N5. The axial Cu1–N5 (2.313(4) Å) bond length is longer than equatorial Cu1–N4 (1.937(4) Å) and Cu–N6 (2.010(4) Å) bond lengths. The bond angles of O2–Cu1–N5 (93.57(14)°), N4–Cu1–N5 (109.57(16)°) and N6–Cu1–N5

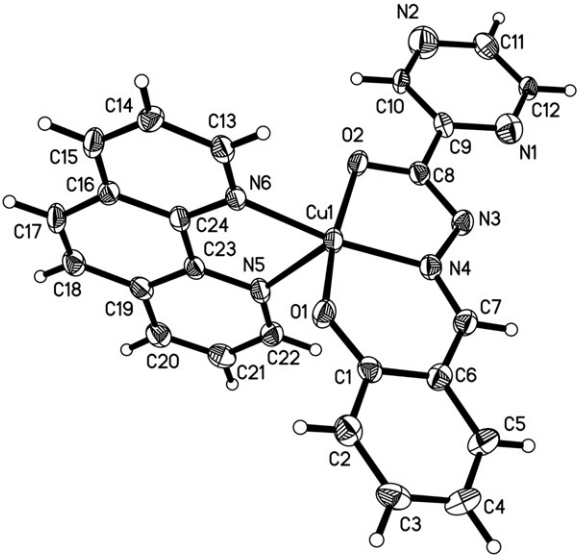


Figure 4. Structure of [CuL^2(phen)] (**2**) with the atom-numbering scheme.

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

Cu(1)–O(1)	1.915(3)	Cu(1)–N(4)	1.937(4)
Cu(1)–O(2)	1.961(3)	Cu(1)–N(6)	2.010(4)
Cu(1)–N(5)	2.313(4)		
O(1)–Cu(1)–N(4)	93.02(15)	O(2)–Cu(1)–N(6)	93.62(14)
O(1)–Cu(1)–O(2)	168.02(15)	O(1)–Cu(1)–N(5)	98.25(15)
N(4)–Cu(1)–O(2)	81.11(15)	N(4)–Cu(1)–N(5)	109.57(16)
O(1)–Cu(1)–N(6)	90.93(15)	O(2)–Cu(1)–N(5)	93.57(14)
N(4)–Cu(1)–N(6)	171.58(17)	N(6)–Cu(1)–N(5)	77.15(15)

(77.15(15)°) indicate distortion from perfect square-pyramidal geometry. The Cu–O and Cu–N distances are comparable to the distances observed in other Cu(II) complexes having the same coordination [22, 23, 30]. Dihedral angle between the pyrazine ring plane and the plane constituted by Cu1, O1, O2, N3, N4, and C1–C8 (mean deviations are in the range 0.0027–0.2450 Å) is 5.66(2)°. The dihedral angle between the phen and the above-mentioned plane is 89.88(4)°.

In the crystal lattice, each [CuL^2(phen)] links to two adjacent molecules *via* two pairs of reciprocal hydrogen bonds between phen C–H and deprotonated amide-O and phenolate-O, giving rise to a 1-D assembly (figure 5). The C···O distances and C–H···O angles are 3.1852 Å and 132°, 3.4256 Å and 150°, respectively.

4. Conclusion

Two Cu(II) complexes with aroylhydrazones, $\{[Cu_2(L^1)_2]\cdot DMF\}_n$ (**1**) and [CuL^2(phen)] (**2**), have been synthesized and structurally characterized. In each complex the planar ligand binds the metal ion *via* phenolate-O, imine-N, and amide-O. Complex **1** is a

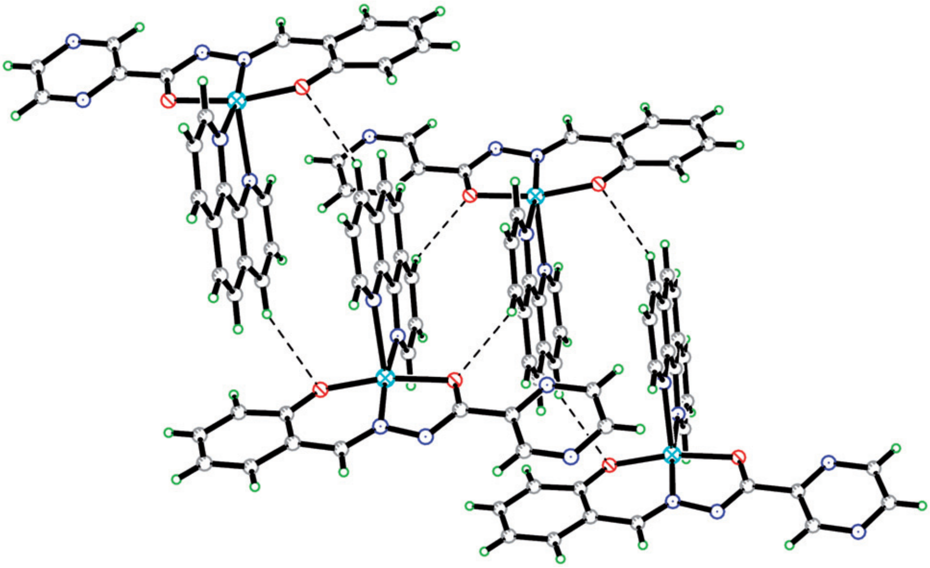


Figure 5. 1-D arrangement of [CuL^2(phen)] (**2**) in the crystal lattice.

polymeric Cu(II) complex of aroylhydrazones *via* equatorial–apical amide-O bridges employing the phenoxo-bridged binuclear Cu(II) units as building blocks. Complex **2** is a monomer where the bidentate phen saturates the square-pyramidal Cu(II) and precludes dimerization observed in other Cu(II) complexes of aroylhydrazones.

Supplementary material

CCDC 880382 and 880383 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 E-mail: deposit@ccdc.cam.ac.uk

Acknowledgments

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