

# Dicopper(II) Schiff base aminobenzoates with discrete molecular and 1D-chain polymeric structures

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## Abstract

Dicopper(II) complexes  $[\text{Cu}_2\text{L}(\text{O}_2\text{CC}_6\text{H}_4\text{-}o\text{-NH}_2)]$  (**1**) and  $[\text{Cu}_2\text{L}(\text{O}_2\text{CC}_6\text{H}_4\text{-}p\text{-NH}_2)]$  (**2**) are prepared from a reaction of  $[\text{Cu}_2\text{L}(\text{O}_2\text{CMe})]$  with the corresponding aminobenzoic acid and a base in MeOH, where L is a trianionic pentadentate Schiff base ligand  $N,N'$ -(2-hydroxypropane-1,3-diyl)bis(salicylalimine). The complexes are structurally characterized by X-ray crystallography. The crystal structures show the presence of an asymmetrically bridged  $\{\text{Cu}_2^{\text{II}}(\mu\text{-OR})(\mu\text{-O}_2\text{CR})\}$  core where the endogenous monoatomic bridging alkoxo group is derived from the Schiff base and the aminobenzoate ligand displays *syn-syn* bridging mode. The Cu...Cu separation and Cu-OR-Cu bond angle in **1** and **2** are 3.472(1) Å, 131.02(18)° and 3.511(1) Å, 132.20(17)°, respectively. The *o*-aminobenzoate complex is discrete dimeric nature. The pendant *o*-amino group is involved in an intramolecular hydrogen bonding interaction with one carboxylate oxygen atom. The crystal structure of the *p*-aminobenzoate species **2** shows the formation of a one-dimensional polymeric chain resulting from the axial binding of the pendant *p*-amino group to one copper center belonging to another dimeric unit. Magnetic studies show that both the complexes are antiferromagnetic in nature giving a singlet-triplet energy separation of -130 and -150  $\text{cm}^{-1}$  for **1** and **2**, respectively. The 1D chain complex **2** magnetically behaves like the discrete dimeric complex **1**.

*Keywords:* Dicopper(II) complex; 1D Coordination polymer; Crystal structure; Magnetic properties; Schiff base

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## 1. Introduction

Binuclear copper(II) complexes are of interest as models for investigating intramolecular magnetic-exchange interactions between two metal centers in different structural motifs, viz. the “paddle-wheel” dicopper(II) tetracarboxylates, symmetrically bridged hydroxo or alkoxo species, and asymmetrically bridged complexes with a  $(\mu\text{-hydroxo/alkoxo})(\mu\text{-carboxylato})$ dicopper(II) core [1–10]. Dicopper(II) complexes are also of importance as precursors in the chemistry of supramolecular and discrete molecular

high-nuclearity copper(II) complexes [11–20]. In our recent publications, we have shown that dicopper(II) complexes containing pentadentate Schiff base ligands  $N,N'$ -(2-hydroxypropane-1,3-diyl)bis(salicylalimine) ( $\text{H}_3\text{L}$ ) or  $N,N'$ -(2-hydroxypropane-1,3-diyl)bis(acetylacetonimine) ( $\text{H}_3\text{L}^1$ ) are useful for the synthesis of high nuclearity copper(II) complexes showing interesting magneto-structural properties [16–20].

We have observed that the dicopper(II) Schiff base complexes having bridging carboxylate like *p*-hydroxycinnamate with a pendant hydroxyl group form helical supramolecular structure due to hydrogen bonding interactions involving one phenoxo oxygen atom of the Schiff base and the hydroxyl group of the carboxylate [21]. In contrast, the *p*-hydroxybenzoate complex is a discrete tetranuclear species resulting from the self-assembly of

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two dicopper(II) units [22]. The present work stems from our interest to prepare analogous dicopper(II) Schiff base ( $H_3L$ ) complexes containing *o*- and *p*-aminobenzoate ligands with an aim to explore the effect of the pendant amino group on the structure and magnetic properties of the complexes. Herein we report the synthesis, crystal structure and magnetic properties of two new dicopper(II) complexes  $[Cu_2L(O_2CC_6H_4\text{-}o\text{-}NH_2)]$  (**1**) and  $[Cu_2L(O_2CC_6H_4\text{-}p\text{-}NH_2)]$  (**2**) having a  $(\mu\text{-alkoxo})(\mu\text{-carboxylato})$ dicopper(II) core. While **1** is discrete dimeric, **2** is a one-dimensional coordination polymer.

## 2. Experimental

### 2.1. Materials and measurements

Chemicals and reagents were procured from commercial sources and were used as received. The Schiff base  $N,N'$ -(2-hydroxypropane-1,3-diyl)bis(salicylalimine) ( $H_3L$ ) and the precursor complex  $[Cu_2L(O_2CMe)]$  were prepared following literature procedures [7]. The elemental analyses were done using Thermo Finnigan FLASH EA 1112 CHN analyser instrument. The infrared and electronic spectra were obtained from Bruker Equinox 55 and Perkin–Elmer Lambda 35 spectrometers, respectively. Variable temperature magnetic susceptibility data for the polycrystalline samples of the complexes in the temperature range 18–300 K were obtained using a Model 300 Lewis Coil Force magnetometer (George Associates Inc., Berkeley, CA), equipped with a closed cycle cryostat (Air Products) and a Cahn balance.  $Hg[Co(NCS)_4]$  was used as a standard. The experimental susceptibility data were corrected for diamagnetic contributions and temperature independent paramagnetism [23]. The magnetic susceptibility data were fitted to the modified Bleaney–Bowers expression by means of a least-squares computer program [23,24]. The Hamiltonian and susceptibility equation used were:  $\hat{H} = -2J\hat{S}_1\hat{S}_2$  ( $S_1 = S_2 = 1/2$  for a  $d^9\text{-}d^9$  dicopper(II) core) and  $\chi_{Cu} = [Ng^2\beta^2/k(T - \theta)][3 + \exp(-2J/k(T - \theta))]^{-1} (1 - \rho) + (Ng_1^2\beta^2/4kT)\rho + N_z$ , where  $\rho$  is the fraction of paramagnetic impurity and  $2J$  is the singlet–triplet energy separation. The expression used to calculate  $R$  value is:  $R = \sum_i \{ \chi_{obs}(T_i) - \chi_{calc}(T_i) \}^2 / \chi_{obs}(T_i)^2$ . The best theoretical fit gave  $2J = -130 \text{ cm}^{-1}$ ,  $g = 2.06$ ,  $\rho = 0.011$ ,  $g_1 = 2.2$ ,  $\theta = 0 \text{ K}$ ,  $R = 6.5 \times 10^{-3}$  for **1** and  $2J = -150 \text{ cm}^{-1}$ ,  $g = 2.19$ ,  $\rho = 0.02$ ,  $g_1 = 2.2$ ,  $\theta = 6 \text{ K}$ ,  $R = 7.9 \times 10^{-3}$  for **2**. The magnetic moments were calculated in  $\mu_B$  unit ( $\mu_B \approx 9.274 \times 10^{-24} \text{ JT}^{-1}$ ).

### 2.2. Synthesis

The complexes were prepared by a common synthetic procedure in which the *ortho*- or *para*-aminobenzoic

acid (0.24 g, 1.7 mmol) taken in methanol (10 ml) was initially treated with piperidine (0.15 ml, 1.5 mmol), followed by reaction with a methanol solution of  $[Cu_2L(O_2CMe)]$  (0.71 g, 1.5 mmol). The solution was refluxed for 30 min, cooled to an ambient temperature and the product, isolated as a green solid, was washed with ethanol and finally dried in vacuum over  $P_4O_{10}$  (~65% yield). *Anal. Calc.* for  $C_{24}H_{21}Cu_2N_3O_5$  (**1**): C, 51.6; H, 3.8; N, 7.5. *Found*: C, 51.3; H, 4.0; N, 7.7%. FT-IR (KBr phase),  $cm^{-1}$ : 3478m, 3351m, 3051w, 2908w, 1635s, 1601m, 1570m, 1538s, 1467m, 1449s, 1397s, 1343m, 1317s, 1261m, 1196m, 1151m, 1110m, 1107w, 1055w, 1030w, 967w, 895w, 862w, 760s, 706m, 671w, 593w, 573w, 469w (s, strong; m, medium; w, weak). Electronic spectral data in MeOH [ $\lambda_{max}$ , nm ( $\epsilon$ ,  $M^{-1}cm^{-1}$ ): 635 (370), 354 (8600), 269 (22600), 242 (42000), 222 (54000)]. Magnetic susceptibility data [ $\chi_M^{corr}$  (per copper),  $cm^3M^{-1}$ ):  $1.17 \times 10^{-3}$  at 300 K;  $0.35 \times 10^{-3}$  at 18 K. Magnetic moment ( $\mu_{eff}$  per copper):  $1.67 \mu_B$  at 300 K and  $0.22 \mu_B$  at 18 K. *Anal. Calc.* for  $C_{24}H_{21}Cu_2N_3O_5$  (**2**): C, 51.6; H, 3.8; N, 7.5. *Found*: C, 51.4; H, 4.0; N, 7.6%. FT-IR (KBr phase),  $cm^{-1}$ : 3419m, 3341m, 3052w, 2925w, 2899w, 1632s, 1600s, 1587s, 1548s, 1449s, 1390s, 1349m, 1319m, 1281m, 1186m, 1167m, 1148m, 1132m, 1055w, 1027w, 966w, 858w, 792m, 758m, 698m, 625w, 587w, 513w, 475w, 437w. Electronic spectral data in MeOH [ $\lambda_{max}$ , nm ( $\epsilon$ ,  $M^{-1}cm^{-1}$ ): 640 (370), 364 (10100), 273 (41600), 242 (43600), 223 (50000)]. Magnetic susceptibility data [ $\chi_M^{corr}$  (per copper),  $cm^3M^{-1}$ ):  $1.29 \times 10^{-3}$  at 300 K;  $0.73 \times 10^{-3}$  at 18 K. Magnetic moment ( $\mu_{eff}$  per copper):  $1.76 \mu_B$  at 300 K and  $0.33 \mu_B$  at 18 K.

### 2.3. X-ray crystallography

Single crystals of the complexes were obtained on slow concentration of the mother liquor at room temperature. The crystals were mounted on glass fibers using epoxy cement. All geometric and intensity data for **1** were collected using an automated Enraf-Nonius CAD4 diffractometer equipped with graphite monochromated Mo  $K\alpha$  radiation. Intensity data were collected using a  $\omega$ - $2\theta$  scan mode and the data were corrected for Lorentz-polarization effects and for absorption [25a]. Intensity data for **2** were measured in frames with increasing  $\omega$  (width of  $0.3^\circ$ /frame) at a scan speed of 12 s/frame using a Bruker SMART APEX CCD diffractometer, equipped with a fine-focus sealed tube X-ray source. The SMART software was used for data acquisition and the SAINT software for data extraction. Empirical absorption correction was made on the data [25b]. The structures were solved by heavy atom method and refined on  $F^2$  by full-matrix least-squares using SHELX programs [26]. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated in their calculated positions, assigned fixed ther-

Table 1

Selected crystallographic data for discrete dimeric [Cu<sub>2</sub>L(O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>-*o*-NH<sub>2</sub>)] (**1**) and 1D-chain polymeric [Cu<sub>2</sub>L(O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>-*p*-NH<sub>2</sub>)] (**2**)

	<b>1</b>	<b>2</b>
Empirical formula	C <sub>24</sub> H <sub>21</sub> Cu <sub>2</sub> N <sub>3</sub> O <sub>5</sub>	C <sub>24</sub> H <sub>21</sub> Cu <sub>2</sub> N <sub>3</sub> O <sub>5</sub>
Formula weight	558.52	558.52
Temperature (K)	293(2)	293(2)
$\lambda$ (Mo K $\alpha$ ) (Å)	0.71073	0.71073
Crystal system	orthorhombic	orthorhombic
Space group (no.)	<i>Pcab</i> (no. 61)	<i>Pbca</i> (no. 61)
<i>Unit cell dimensions</i>		
<i>a</i> (Å)	16.920(2)	9.3620(11)
<i>b</i> (Å)	11.017(5)	18.642(2)
<i>c</i> (Å)	24.199(4)	25.440(3)
<i>V</i> (Å <sup>3</sup> )	4511(2)	4440.1(9)
<i>Z</i>	8	8
<i>D</i> <sub>calc</sub> (Mg m <sup>-3</sup> )	1.645	1.671
Absorption coefficient (mm <sup>-1</sup> )	1.928	1.959
<i>F</i> (000)	2272	2272
Crystal size (mm)	0.32×0.32×0.2	0.27×0.11×0.03
$\theta$ Range for data collection (°)	1.68–25.0	1.60–23.25
Index ranges	0 ≤ <i>h</i> ≤ 20, 0 ≤ <i>k</i> ≤ 13, 0 ≤ <i>l</i> ≤ 28	−10 ≤ <i>h</i> ≤ 10, −20 ≤ <i>k</i> ≤ 20, −28 ≤ <i>l</i> ≤ 25
Reflections collected [ <i>R</i> <sub>int</sub> ]	3965 [0.0000]	25870 [0.0806]
Reflections observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	3965 [2738]	3173 [2157]
Number of parameters refined	315	315
Maximum and minimum transmission	0.6798, 0.5347	0.7572, 0.6114
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.109	0.834
<i>R</i> (observed data) [ <i>R</i> (all data)]	0.0590 [0.0988]	0.0384 [0.0686]
<i>R</i> <sub>w</sub> (observed data) [ <i>R</i> <sub>w</sub> (all data)]	0.1097 [0.1240]	0.0760 [0.0845]
Largest difference peak and hole (e Å <sup>-3</sup> )	0.486 and −0.332	0.352 and −0.407
Weight factor: <i>w</i> = 1/[ $\sigma^2(F_o^2) + (AP)^2 + BP$ ]	<i>A</i> = 0.0562, <i>B</i> = 2.4706	<i>A</i> = 0.0441, <i>B</i> = 1.8437

mal parameters and refined using a riding model. They were used for structure factor calculation only. Selected crystallographic data are given in Table 1. Perspective views of the complexes were obtained by ORTEP [27].

### 3. Results and discussion

#### 3.1. Synthesis and general properties

Complexes **1** and **2** are prepared in high yield by reacting [Cu<sub>2</sub>L(O<sub>2</sub>CMe)] with the respective *ortho*- and *para*-aminobenzoate ligand in methanol. The complexes show a visible spectral band near 640 nm in MeOH, assignable to the d–d transition. The infrared spectra display characteristic bands for the amino group near 3450 and 3350 cm<sup>-1</sup>. The IR spectral band for the imine group [ $\nu$ (C=N)] is observed near 1640 cm<sup>-1</sup>.

#### 3.2. Crystal structures

The molecular structures of **1** and **2** are obtained from single crystal X-ray crystallographic studies. Selected bond distances and angles are listed in Table 2 and the ORTEP views are given in Figs. 1 and 2. Complex **1** is a discrete dimeric species in which the metal atoms are bonded to a pentadentate Schiff base and a carboxylate ligand. The Schiff base provides the endo-

genic alkoxo bridge, while the carboxylate displays three-atom bridging mode in the {Cu<sub>2</sub>( $\mu$ -OR)( $\mu$ -O<sub>2</sub>CR)} core. Each copper has CuNO<sub>3</sub> square-planar coordination geometry. The Cu···Cu distance and Cu–O–Cu angle are 3.472(1) Å and 131.02(18)°, respectively. The copper atoms are deviated by ~0.01 Å from the basal plane. The alkoxo oxygen atom O(2) has a planar geometry as the sum of three angles is ~359°. The pendant *o*-amino group is involved in moderately strong intramolecular hydrogen bonding interaction with the oxygen atom O(4) of the carboxylate [N(3)···O(4), 2.65(1) Å].

Complex **2** with *p*-aminobenzoate ligand forms a one-dimensional coordination polymer in which the [Cu<sub>2</sub>L(O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>-*p*-NH<sub>2</sub>)] units are linked via axial coordination of the amino group of one unit to the copper center of another dimeric unit. The Cu(1) atom has a square pyramidal (4+1) coordination geometry, while the Cu(2) atom is square planar. The Cu···Cu distance and Cu–O–Cu angle are 3.511(1) Å and 132.20(17)°, respectively. The Cu(1) atom is deviated by ~0.1 Å from the basal plane due to the formation of the axial bond. The polymeric structure of **2** displays an isotactic arrangement of the Cu(2) atom protruding to one side of the polymeric chain that contains the Cu(1) atom. The polymeric structure of **2** is significantly different from its isonicotinate analogue Cu<sub>2</sub>L(O<sub>2</sub>CC<sub>5</sub>H<sub>4</sub>N)] in which the Cu<sub>2</sub>L<sup>+</sup> units are covalently linked by the

Table 2

Selected bond distances (Å) and angles (°) for discrete dimeric  $[\text{Cu}_2\text{L}(\text{O}_2\text{CC}_6\text{H}_4\text{-}o\text{-NH}_2)]$  (**1**) and 1D-chain polymeric  $[\text{Cu}_2\text{L}(\text{O}_2\text{CC}_6\text{H}_4\text{-}p\text{-NH}_2)]$  (**2**)

	<b>1</b>	<b>2</b>
Cu(1)···Cu(2)	3.472(1)	3.511(1)
Cu(1)–O(1)	1.905(3)	1.891(3)
Cu(1)–O(2)	1.914(3)	1.927(3)
Cu(1)–O(5)	1.932(3)	1.974(3)
Cu(1)–N(1)	1.941(4)	1.943(4)
Cu(1)–N(3)#1 <sup>a</sup>		2.552(5)
Cu(2)–O(2)	1.901(3)	1.913(3)
Cu(2)–O(3)	1.886(4)	1.892(3)
Cu(2)–O(4)	1.925(4)	1.927(3)
Cu(2)–N(2)	1.927(5)	1.926(4)
Cu(1)–O(2)–Cu(2)	131.02(18)	132.20(17)
O(1)–Cu(1)–O(2)	176.47(15)	177.23(14)
O(1)–Cu(1)–O(5)	87.35(15)	89.25(14)
O(1)–Cu(1)–N(1)	92.44(16)	93.14(15)
O(2)–Cu(1)–O(5)	96.17(14)	93.45(13)
O(2)–Cu(1)–N(1)	84.04(16)	84.09(15)
O(5)–Cu(1)–N(1)	179.39(17)	166.22(15)
O(2)–Cu(2)–O(3)	178.55(16)	175.24(14)
O(2)–Cu(2)–O(4)	94.83(14)	94.61(13)
O(2)–Cu(2)–N(2)	84.16(16)	84.47(15)
O(3)–Cu(2)–O(4)	86.32(16)	88.38(14)
O(3)–Cu(2)–N(2)	94.65(18)	93.09(15)
O(4)–Cu(2)–N(2)	177.44(17)	171.87(15)

<sup>a</sup> Symmetry operation (#1):  $x-1, y, z$ .

pyridine nitrogen atom of the isonicotinate ligand to give a syndiotactic arrangement of the copper ions protruding outside the chain [28].

### 3.3. Magnetic properties

The variable temperature magnetic susceptibility data for the complexes in the temperature range 300–18 K show an antiferromagnetic (AF) behavior of the com-

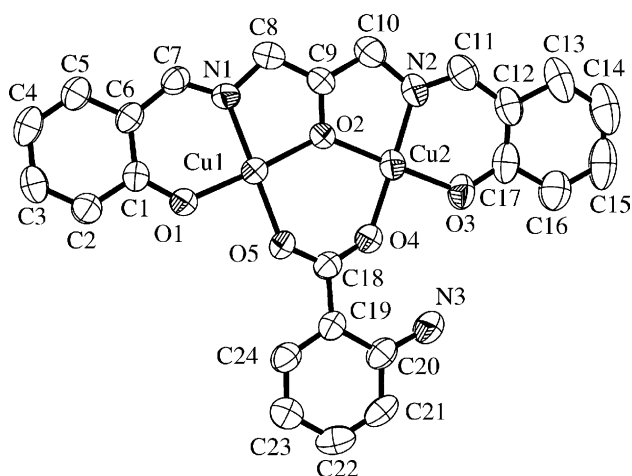


Fig. 1. An ORTEP view of  $[\text{Cu}_2\text{L}(\text{O}_2\text{CC}_6\text{H}_4\text{-}o\text{-NH}_2)]$  (**1**) showing 50% probability thermal ellipsoids and the atom labeling scheme.

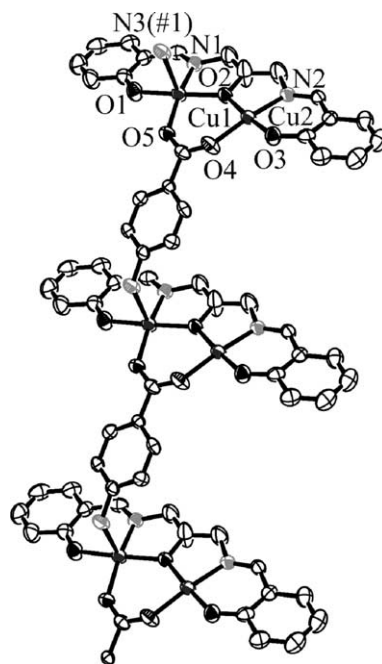


Fig. 2. An ORTEP view of the one-dimensional chain polymeric complex  $[\text{Cu}_2\text{L}(\text{O}_2\text{CC}_6\text{H}_4\text{-}p\text{-NH}_2)]$  (**2**) showing 50% probability thermal ellipsoids and the atom numbering scheme.

plexes (Fig. 3). The magnetic moment values (per copper) of  $\sim 1.7 \mu_B$  at 300 K and  $\sim 0.3 \mu_B$  at 18 K indicate significant AF spin–spin coupling in the asymmetrically bridged dicopper(II) core. A theoretical fitting of the magnetic susceptibility data for **1** gave the singlet–triplet energy separation ( $-2J$ ) of  $130 \text{ cm}^{-1}$  with the singlet as the ground state. Complex **1** is a discrete dimeric species and the observed magnitude of the exchange coupling constant compares well with that of the precursor complex ( $-170 \text{ cm}^{-1}$ ) [7]. The nature and magnitude of the magnetic exchange interaction in the  $\{\text{Cu}_2(\mu\text{-OR})(\mu\text{-$

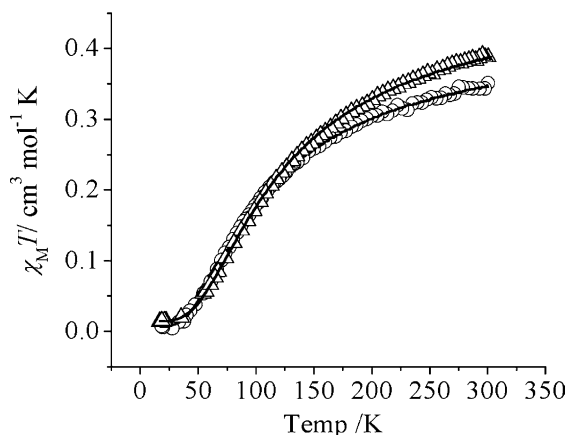


Fig. 3. Plots of  $\chi_M T$  vs.  $T$  for the polycrystalline samples of  $[\text{Cu}_2\text{L}(\text{O}_2\text{CC}_6\text{H}_4\text{-}o\text{-NH}_2)]$  (**1**,  $\circ$ ) and 1D-chain polymeric  $[\text{Cu}_2\text{L}(\text{O}_2\text{CC}_6\text{H}_4\text{-}p\text{-NH}_2)]$  (**2**,  $\Delta$ ). The solid lines are the theoretical fits to the experimental data.

O<sub>2</sub>CR)} core primarily depends on the Cu–O–Cu angle. The magnitude of  $-2J$  in such a core is generally small due to counter-complimentary nature of overlap of the magnetic orbitals [4,5,7].

The magnetic behavior of the 1D chain coordination polymer **2** is similar to those observed for the discrete dicopper(II) complexes with a {Cu<sub>2</sub>(μ-OR)(μ-O<sub>2</sub>CR)} core. Complex **2** has been modeled as an isolated dimeric species and good theoretical fitting of the magnetic susceptibility data is obtained using modified Bleaney–Bowers expression [23,24]. The  $2J$  value is  $-150\text{ cm}^{-1}$  with a  $\theta$  value of 6 K. While an antiferromagnetic coupling is predominant in the dicopper(II) unit having a large Cu–O–Cu angle of 132°, a positive value of  $\theta$  suggests the presence of minor ferromagnetic interaction involving the dimeric units through the axial bond. The involvement of the  $d_{x^2-y^2}$  orbital of the Cu(1) atom and the  $d_{z^2}$  orbital of the adjacent copper atom along the chain could promote weak ferromagnetic interaction. The magnetic behavior of **2** is significantly different from that of the isonicotinate complex [Cu<sub>2</sub>L(O<sub>2</sub>CC<sub>5</sub>H<sub>4</sub>N)]<sub>x</sub> for which the magnetic data do not show any good fit with the Bleaney–Bowers expression. The magnetic model assumes the isonicotinate complex as an equimolar mixture of copper atoms belonging to an antiferromagnetically coupled one-dimensional Heisenberg chain with the other copper atoms outside the chain behaving like paramagnetic centers [28]. The 1D chain of **2** magnetically behaves like the discrete dimeric complex **1**.

In summary, two new Schiff base copper(II) complexes having asymmetrically bridged dicopper(II) cores are prepared and structurally characterized. The *o*-aminobenzoate complex is discrete dimeric in nature. The *p*-aminobenzoate species shows the formation of a one-dimensional coordination polymer. The dicopper(II) cores in the complexes show antiferromagnetic magnetic exchange. The magnetic interaction between two copper centers along the 1D chain in **2** is weakly ferromagnetic in nature.

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## Appendix A. Supplementary data

Crystallographic data for **1** and **2** in the CIF format have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 240088 and 240089.

Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-366-033; e-mail: deposit@ccdc.ac.uk or <http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.poly.2004.06.014.

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