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Inorganica Chimica Acta 357 (2004) 1077-1082

Inorganica Chimica Acta

www.elsevier.com/locate/ica

# Synthesis, crystal structure and magnetic properties of quasi-linear tetranuclear copper(II) Schiff base complexes formed by covalent linkage of asymmetrically dibridged dicopper(II) units <sup>☆</sup>

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Received 14 June 2003; accepted 4 October 2003

# Abstract

Alkoxo-phenoxo bridged tetranuclear copper(II) complexes  $[Cu_4L_2(O_2CC_6H_4-p-OH)_2]$  (1) and  $[Cu_4L_2(O_2CC_6H_4-o-OH)_2]$  (2) containing pentadentate Schiff base ligand N, N'-(2-hydroxypropane-1,3-diyl)bis(salicylaldimine) (H<sub>3</sub>L) are prepared and structurally characterized. Crystal structures of the complexes show the covalent linkage between two { $Cu_2L(O_2CR)$ }( $R = C_6H_4-p-OH$ ,  $C_6H_4-o-OH$ ) units through the phenoxo atoms of the Schiff base ligand showing axial/equatorial bonding modes. The Cu(1)–O(2)–Cu(2) alkoxo bridge angle is 131° in 1 and 2. The pendant *ortho-* and *para-* OH groups of the three-atom bridging carboxylate ligands show no apparent bonding interactions with the metal or other group(s). The complexes show a d–d band near 635 nm in CH<sub>2</sub>Cl<sub>2</sub>. Variable temperature magnetic susceptibility measurements in the temperature range 300–18 K show antiferromagnetically coupled spin system. A theoretical fit of the magnetic data using exchange parameters  $J_1$  and  $J_2$  for the intradimer and interdimer units of the quasi-linear tetrameric core gave values as:  $J_1 = -132$ ,  $J_2 = -72$  cm<sup>-1</sup> for 1 and  $J_1 = -167$ ,  $J_2 = -67$  cm<sup>-1</sup> for 2. © 2003 Elsevier B.V. All rights reserved.

Keywords: Copper complexes; Crystal structures; Pentadentate Schiff base; Magnetic properties

# 1. Introduction

Dinuclear copper(II) complexes have been extensively used to derive magneto-structural correlations to understand the nature of spin–spin coupling phenomena in different structural arrangements and as precursors in the synthesis of high nuclearity copper clusters showing novel supramolecular structural features [1–6]. Among three major dinuclear copper(II) structural types, the asymmetrically dibridged dicopper(II) complexes with a  $\{Cu_2(\mu-OH/OR)(\mu-O_2CR)^{2+}\}$  core have drawn considerable current interests for their use in catalytic reactions, in modeling the dicopper active sites of hemocyanin and to probe their unusually low magnitude of the exchange parameter (-2*J*) which is proposed to be due to the 'counter-complementary' nature of overlap of the monoatomic bridging hydroxo/alkoxo and the three-atom bridging carboxylato ligands [7–10]. This is in contrast with the complementary effect of the overlap known for the other two classes of dicopper(II) complexes having  $\{Cu_2(\mu-OH/OR)_2^{2+}\}$  and  $[Cu_2(\mu-O_2CR)_4]$  cores [11–14].

Multi-dentate Schiff base ligands have generally been used to stabilize the asymmetrically dibridged dicopper(II) core. The present work stems from our interest to study the magneto-structural properties of dinuclear complexes having a pentadentate Schiff base N, N'-(2-hydroxypropane-1,3-diyl)bis(salicylaldimine) (H<sub>3</sub>L) using *ortho*- and *para*-substituted benzoic acid for generation of possible supramolecular architectures utilizing the pendant phenolic OH groups. Earlier

<sup>&</sup>lt;sup>\*</sup> Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2003.10.011.

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Nishida and Kida have shown that this Schiff base ligand in presence of benzoic acid forms a discrete dimeric species, structurally characterized as [Cu<sub>2</sub>L(O<sub>2</sub> CPh)] [7]. Interestingly, using substituted benzoic acids, we are successful in isolating new tetrameric copper(II) complexes of formulations [Cu<sub>4</sub>L<sub>2</sub>(O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>-*p*-OH)<sub>2</sub>] (1) and  $[Cu_4L_2(O_2CC_6H_4-o-OH)_2]$  (2), resulting from the covalent linkage of two dimeric  $\{Cu_2L(O_2CR)\}$ units. While several types of tetranuclear copper(II) complexes are known showing a variety of arrangements of four copper(II) centers like linear [15–19], cubane [20-22], rectangular [23-25], and cyclic [26-29], the linear complexes are of particular importance for NLO applications [15]. Herein, we report the synthesis, crystal structure and magnetic properties of complexes 1 and 2. Significant result of this study is the observation of a quasi-linear tetrameric copper(II) core having pendant phenolic OH groups that could be utilized for suitable binding to a metal center or in the formation of supramolecular architecture.

# 2. Experimental

# 2.1. Materials

All chemicals used were of reagent grade and purchased from commercial sources. The Schiff base N, N'-(2-hydroxypropane-1,3-diyl)bis(salicylaldimine) (H<sub>3</sub>L) and the precursor complex [Cu<sub>2</sub>L(O<sub>2</sub>CMe)] were prepared by literature procedures [7]. The solvents used in the spectral measurements were distilled prior to use.

## 2.2. Synthesis of the complexes

 $[Cu_4L_2(O_2CC_6H_4-p-OH)_2]$  (1) Complexes and  $[Cu_4L_2(O_2CC_6H_4-o-OH)_2]$  (2) were prepared by a general preparative method in which the carboxylic acid (0.2 g, 1.45 mmol) was initially reacted with sodium hydroxide (0.05 g, 1.25 mmol) under stirring for 30 min in 10 ml MeOH. The sodium salt of the carboxylate was then reacted with  $[Cu_2L(O_2CMe)]$  (0.7 g, 1.4 mmol) under stirring for a period of 2 h. A green solid thus formed was separated, washed with ethanol and finally dried over  $P_4O_{10}$  in vacuo. Yield: 0.6 g (65%). Anal. Found: C, 51.3; H, 3.9; N, 4.7. Calc. for C<sub>48</sub>H<sub>40</sub> N<sub>4</sub>O<sub>12</sub>Cu<sub>4</sub> (1): C, 51.5; H, 3.6; N, 5.0%. FT-IR (KBr phase), cm<sup>-1</sup>: 3388br, 3021w, 2911w, 1643s, 1600s, 1550s, 1448s, 1394s, 1300m, 1198m, 1153m, 1053w, 857w, 759m, 699m, 637w, 571w, 461w, 426w [s, strong; m, medium; w, weak; br, broad]. UV–vis in MeOH,  $\lambda_{max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 640 (390), 362 (8500), 268 (27500), 243 (43000). Anal. Found: C, 51.21; H, 3.78; N, 4.87. Calc. for C<sub>48</sub>H<sub>40</sub>N<sub>4</sub>O<sub>12</sub>Cu<sub>4</sub> (2): C, 51.52; H, 3.60; N, 5.01%. FT-IR (KBr phase), cm<sup>-1</sup>: 3442br, 3021w, 2908w, 1635s, 1583s, 1535s, 1449s, 1329s, 1312s, 1196m, 1149m, 1032w, 758s, 702m, 593w, 440w. UV–vis in MeOH,  $\lambda_{max}$ , nm ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 631 (280), 365 (10500), 272 (38500).

### 2.3. Measurements

The infrared and electronic spectral data were recorded on a Bruker Equinox-55 FT-IR and Hitachi U-3400 spectrophotometers, respectively. Elemental analysis data were obtained from Heraeus CHN–O rapid instrument. Variable temperature magnetic susceptibility data for the powdered samples of complexes 1 and 2 were measured in the temperature range 18–300 K using a Model 300 Lewis Coil Force Magnetometer (George Associates Inc., Berkeley, CA), equipped with a Cahn balance and a closed cycle cryostat (Air Products). The experimental susceptibility data were corrected for diamagnetic contributions and for temperature-independent paramagnetism (N<sub> $\alpha$ </sub>). Hg[Co(NCS)<sub>4</sub>] was used as a standard.

# 2.4. X-ray crystallography

Single crystals of complex 1 were obtained by slow evaporation of methanol-isopropanol solution (6:1 v/v) at an ambient temperature. Single crystals of 2 were obtained from the mother liquor on slow evaporation. Crystal mounting was done on glass fiber using epoxy cement. All geometric and intensity data were collected using an automated Enraf-Nonius CAD4 diffractometer equipped with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Intensity data, collected using  $\omega$ -2 $\theta$  scan mode, were corrected for Lorentz-polarization effects and for absorption [30]. The structures were solved by heavy atom method and refined on  $F^2$  by full matrix least squares using SHELX programs [31]. There was one lattice isopropanol molecule in the asymmetric unit of the crystal structure of 1. The non-hydrogen atoms other than two carbon atoms of the solvent molecule in 1 and the positionally disordered hydroxy oxygen atom of the carboxylate in 2 were refined anisotropically. The O(6) and O(6A) atoms were refined with a site occupancy factor of 0.6 and 0.4, respectively. Few hydrogen atoms were located from the difference Fourier map and the rest were generated and assigned fixed thermal parameters, and refined using riding model. The hydrogen atoms were used for structure factor calculation only. Selected crystallographic data are given in Table 1. Perspective views of the molecules were obtained by ORTEP [32].

# 3. Results and discussion

#### 3.1. Synthesis and general aspects

The tetranuclear complexes are prepared in high yield from a reaction of  $[Cu_2L(O_2CMe)]$  with the sodium salt

Table 2

in complex 1.2<sup>i</sup>PrOH and 2

Table 1 Crystallographic data for **1**.2<sup>i</sup>PrOH and **2** 

	1.2 <sup>i</sup> PrOH	2
Empirical formula	C54H56Cu4N4O14	$C_{48}H_{40}Cu_4N_4O_{12}$
Formula weight	1239.19	1119.0
Temperature (K)	293(2)	293(2)
$\lambda$ (Mo Ka) (Å)	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group (no.)	$P\overline{1}(2)$	$P2_1/n(14)$
Unit cell dimensions		, , ,
a (Å)	9.943(3)	11.680(4)
b (Å)	11.721(4)	11.1939(15)
<i>c</i> (Å)	11.776(10)	17.798(5)
α (°)	90.21(4)	90
β (°)	100.48(4)	107.04(2)
γ (°)	104.01(3)	90
Volume (Å <sup>3</sup> )	1307.7(12)	2224.7(10)
Ζ	1	2
$\rho_{\text{calc}}$ (Mg/m <sup>-3</sup> )	1.574	1.670
$\mu (\text{mm}^{-1})$	1.675	1.957
F(000)	636	1136
Crystal size, mm <sup>3</sup>	$0.56 \times 0.34 \times 0.15$	$0.56 \times 0.5 \times 0.3$
$\theta$ Range (°)	1.76-25.02	1.87-25.00
(data collection)		
Index ranges	$0 \leq h \leq 11$ ,	$0 \leq h \leq 13$ ,
	$-13 \leq k \leq 13$	$0k \leq 13$
	$-13 \leq l \leq 13$	$-21 \leq l \leq 20$
Reflections collected [R <sub>int</sub> ]	4869 [0.1000]	4114 [0.0921]
Independent reflections	4580 [3114]	3908 [2998]
$[I > 2\sigma(I)]$		
No. of parameters refined	384	354
Maximum, minimum	0.5973, 0.3946	0.5542, 0.4175
transmission		
Goodness-of-fit on $F^2$	1.020	1.077
$R_1[I > 2\sigma(I)][wR_2]$	0.0731 [0.1785]	0.0561 [0.1506]
$R_1(\text{all data}) [wR_2]$	0.1083 [0.2039]	0.0788 [0.1703]
Largest difference peak	1.38 and -0.86	0.93 and -1.02
and hole ( $e Å^{-3}$ )		
Weight factor:	a = 0.1346	a = 0.1023
$w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$		
	b = 0.2937	b = 3.9281

of the *ortho-* or *para-*hydroxybenzoic acid. The precursor complex has a dicopper(II) unit linked by the alkoxide and acetate oxygen atoms [7]. Each copper is coordinated to one nitrogen and two oxygen atoms of the Schiff base and one oxygen of the acetate to form a square planar geometry. Substitution of acetate by the *o-* or *p*-hydroxybenzoate leads to the formation of the tetrameric complexes that are characterized by X-ray crystallography. The infrared spectra of the complexes show characteristic phenolic OH stretch at  $\sim$ 3400 cm<sup>-1</sup>. The complexes display visible spectral band near 635 nm.

### 3.2. Crystal structures

The molecular structures of the complexes have been determined by single crystal X-ray diffraction studies. Relevant bond distances and angles are given in Table 2, and the ORTEP diagrams are shown in Figs. 1 and 2.

 $Cu(1) \cdots Cu(2)$ 3.485(3) 3.481(2)  $Cu(1) \cdots Cu(1) \# 1$ 3.170(3)3.256(2) Cu(1)-O(1) 1.933(5) 1.917(4) Cu(1) - O(2)1.926(5) 1.919(4) Cu(1)-O(5) 1.932(5) 1.953(4) Cu(1) - N(1)1.930(5)1.934(5)Cu(1)-O(1)#1 2.402(5)2.482(5)1.896(5) 1.905(4) Cu(2) - O(2)1.894(4) Cu(2)-O(3) 1.916(5) Cu(2)-O(4) 1.919(4) 1.937(4) 1.922(5) Cu(2) - N(2)1.932(6)Cu(1)-O(2)-Cu(2) 131.5(2) 131.1(2) Cu(1)-O(1)-Cu(1)#1 93.37(18) 94.72(16) O(1)-Cu(1)-O(2) 173.7(2)175.53(17) O(1)-Cu(1)-O(5)89.53(19) 88.03(15) 86.63(18) 85.27(15) O(1)-Cu(1)-O(1)#1 O(1)#1-Cu(1)-O(2)98.13(19) 97.90(15) O(1)#1-Cu(1)-O(5) 89.25(19) 83.77(14) O(1)-Cu(1)-N(1)91.7(2) 92.54(18) O(1)#1-Cu(1)-N(1) 97.3(2) 104.15(16) O(2)-Cu(1)-O(5) 94.55(19) 95.44(16) O(2)-Cu(1)-N(1) 83.8(2) 83.64(18) O(5)-Cu(1)-N(1)173.4(2) 172.08(18) O(2)-Cu(2)-O(3) 176.55(19) 177.50(19) O(2)-Cu(2)-O(4) 96.1(2) 95.45(16) O(2)-Cu(2)-N(2) 84.1(2) 84.16(18) O(3)-Cu(2)-O(4) 87.3(2) 86.25(18) O(3)-Cu(2)-N(2) 92.5(2) 94.39(19) O(4)-Cu(2)-N(2) 175.4(2) 172.6(2)

Selected bond distances (Å) and angles (°) of coordination polyhedra

2

1.2<sup>i</sup>PrOH

Symmetry transformations used to generate equivalent atoms: #1: 1 - x, 1 - y, -z for 1; 1 - x, 1 - y, 1 - z, for 2.



Fig. 1. An ORTEP view of complex 1 with 50% probability thermal ellipsoids showing the atom numbering scheme.

The complexes are formed from the dinuclear precursor complex [Cu<sub>2</sub>L(O<sub>2</sub>CMe)] by substitution of the acetate by *ortho-* and *para-*hydroxy benzoic acids and the resulting {Cu<sub>2</sub>L(O<sub>2</sub>CR)} ( $\mathbf{R} = C_6H_4$ -*p*-OH,  $C_6H_4$ -*o*-OH) unit self assembles to the tetranuclear complex by



Fig. 2. An ORTEP view with 50% probability thermal ellipsoids for complex 2 displaying the atom numbering scheme. The O(6) and O(6a) atoms are positionally disordered with a site occupancy factor of 0.6 and 0.4, respectively.

covalent linkage through the phenoxo oxygen atom of the Schiff base by axial ligation. Both the complexes are centrosymmetric showing a dimeric unit in the crystallographic asymmetric unit. Within the dimeric unit, the dicopper(II) core is bridged by the mono-atomic alkoxo oxygen and the three-atomic carboxylato oxygen atoms retaining the asymmetrically dibridged structure of the precursor complex. The  $Cu(1) \cdot \cdot \cdot Cu(2)$  distance of 3.48 A in 1 and 2 is similar to the  $Cu \cdots Cu$  distance in  $[Cu_2L(O_2CPh)]$  [7]. The other structural features also resemble with the benzoate species except that the Cu(1)center in the tetrameric complexes has a square pyramidal (4+1) CuNO<sub>4</sub> coordination geometry. The basal planes at Cu(1) and Cu(2) centers are essentially planar (dihedral angle:  $11.5^{\circ}$  for 1;  $9.0^{\circ}$  for 2). The alkoxo oxygen atom O(2) has a planar geometry. The Cu(1)-O(2)–Cu(2) angle of  $\sim$ 131° is marginally smaller than the 133° reported for the benzoato dicopper species.

In the Cu(1)Cu(1)'O(1)O(1)' unit, the Cu(1)-O(1)axial bond length of  $\sim 2.45$  Å is considerably long and such a distance is likely to reduce the spin–spin coupling between Cu(1) and Cu(1)' centers. The Cu(1) $\cdots$ Cu(1)' distance is 3.170 (3) Å. The phenoxo-bridge angle Cu(1)-O(1)-Cu(1)' of 93.37 (18)° is significantly lower than the Cu-OR-Cu angles reported for dialkoxo bridged dicopper(II) complexes with a Cu<sub>2</sub>O<sub>2</sub> unit. Kida and coworkers [33] have studied the effects of structural factors on the magnetism of di-µ-alkoxodicopper(II) complexes. They have shown that the Cu–O–Cu angle has the major effect on the exchange parameter (J) value. The other factors like the dihedral angle between two coordination planes, planarity of the  $Cu_2O_2$  unit, and tilt of the O-C bond at the bridging oxygen atom play minor but significant role in the exchange process. The  $Cu_2O_2$  unit in 1 and 2 is planar with the phenoxo oxygen atom O(1) having a planar geometry. The  $Cu_2O_2$ plane makes an angle of  $86.2^{\circ}$  with the O(1), O(2), O(5), and N(1) basal plane. The Cu(1) atom is displaced 0.08 A from this basal plane. Weak axial contact between Cu(2) and O(3) atoms gives rise to a staircase type network structure in the complexes. The complexes



Fig. 3. Crystal packing diagram of **1** along *a*-axis showing the formation of hydrogen bonds involving O(6) atom of the complex and the O(7) atom of the lattice isopropanol solvent molecule (a). A packing diagram of the complexes showing the formation of a staircase structure involving weak axial contact between the copper and oxygen atoms. Only the skeletal structure is shown for clarity (b).

show interesting hydrogen bonding interactions in the crystal packing diagrams (Fig. 3). The hydrogen-bonding interactions in 1 involve the isopropanol molecule and the phenolate oxygen of the Schiff base bound to the terminal copper atom. A significant structural observation is the non-involvement of the *ortho-* and *para*-hydroxy groups of the bridging carboxylates in covalent bonding with other atom(s) or group.

# 3.3. Magnetic properties

The magnetic susceptibility data for the complexes in the temperature range 300–18 K reveal overall antiferromagnetic behavior. Complex 1 gives a magnetic moment (per copper) that varies from 1.72  $\mu_B$  at 300 K to 0.34  $\mu_B$  at 18 K. The  $\mu_{eff}$ /Cu values of 2 are 1.75  $\mu_B$  at 300 K and 0.21  $\mu$ B at 18 K. The data are indicative of a diamagnetic ground state although at 300 K the complex is essentially paramagnetic in nature. The magnetic sus-



Fig. 4. A plot of magnetic susceptibility data in the form of  $\chi_{\rm M}(O)$  and  $\chi_{\rm M}T(\nabla)$  vs. *T* for complex **1** in the temperature range 18–300 K. The theoretical fit to experimental data is shown by solid line.



Fig. 5. Magnetic susceptibility data plotted in the form of  $\chi_{\rm M}(O)$  and  $\chi_{\rm M}T(\Delta)$  vs. *T* for complex **2** in the temperature range 18–300 K. The theoretical fit to the experimental data is shown by solid line.

ceptibilities are shown as a function of temperature in Figs. 4 and 5. The experimental data are fitted for a theoretical model based on Heisenberg spin-1/2 Hamiltonian with nearest neighbor antiferromagnetic interaction [34] using two different coupling constants  $J_1$  and  $J_2$  for the terminal {Cu(2), Cu(1)};{Cu(1)', Cu(2)'} and central {Cu(1), Cu(1)'} dicopper(II) units, in the form as,

$$H = -J_1(S_1S_2 + S_3S_4) - J_2S_2S_3.$$
<sup>(1)</sup>

The spin labels  $S_1, S_2, S_3, S_4$  correspond to the copper atoms Cu(2), Cu(1), Cu(1)', Cu(2)' as shown in the crystal structures. The energy levels are calculated by exact diagonalization of the Hamiltonian matrix set up in the constant total  $M_S$  basis [35]. Using the spin–spin correlation function, the expectation value of  $S_{total}^2$  has been evaluated along with the identification of the total spin of each eigen state. The ground and the first excited state are found to be a singlet and a triplet state, respectively. The magnetic susceptibility has been calculated as  $\chi = M/H$ , where 'H' is the magnetic field and M is the magnetization due to the field applied. The magnetization is evaluated using the following expression:

$$M = [\Sigma_{i}M_{i} \exp(-E_{i}(H)/k_{B}T)/\exp(-E_{i}(H)/k_{B}T)], \quad (2)$$

where  $E_i(H) = E_i^{(0)} + gM_iH$ .  $E_i^{(0)}$  is the eigenvalue of the spin in the eigenstate 'i' and 'g' is the gyromagnetic ratio. Since the value of 'g' depends on the local chemical environment, the 'g' value is varied within 1.98 to 2.2, instead of taking the free electron 'g' value in the fitting. The best theoretical fit gave average g -value as 2.1 for 1 and 2.05 for 2. The presence of a trace quantity of paramagnetic impurity  $(\rho)$  in the analytically pure sample has been taken care of using a Curie-like contribution to the susceptibility in the form  $\chi = C/T$ , where 'C' is a constant. The  $\rho$  values are 0.03% for 1 and 0.6% for **2**. The theoretical model gave excellent fit to the experimental data with *R*-value of  $2.3 \times 10^{-4}$  for 1 and  $5.1 \times 10^{-4}$  for **2**. The magnitudes of the exchange parameters are:  $J_1 = -132$  cm<sup>-1</sup>;  $J_2 = -72$  cm<sup>-1</sup> for complex **1** and  $J_1 = -167$  cm<sup>-1</sup>;  $J_1 = -67$  cm<sup>-1</sup> for complex 2. The magnitude of the  $J_1$  parameter is similar to the values observed for the dimeric precursor complex. The extent of exchange interaction in the phenoxo bridged  $Cu_2O_2$  unit is less due to poor overlap of the metal orbitals with the axially/equatorially bound oxygen atom. A lower magnitude of the Cu-O-Cu angle also weakens the antiferromagnetic (AF) interaction between the copper centers. The singlet ground state results from the alignment of spins in the quasi-linear arrangement of metal atoms as:  $Cu(2)\uparrow -Cu(1)\downarrow Cu(1)' \uparrow -Cu(2)' \downarrow$ . The greater magnitude of  $J_1$  in complex 2 than in 1 could be due to the reduced extent of "counter-complimentary" effect in 2 [7,9]. It is likely that the o-hydroxy group in 2 can form hydrogen bond with the carboxylate oxygen atom. The presence of such a bond is proposed from the longer Cu–O (carboxylato) distances in 2 than in 1.

# 4. Conclusion

Two new quasi-linear tetranuclear copper(II) Schiff base complexes are prepared by covalent linkage of the dimeric precursor involving phenoxo bridges in the presence of o- or p-hydroxybenzoic acid which shows three-atom bridging mode. Both the complexes display staircase like array in the crystal structure. The variable temperature magnetic susceptibility data show antiferromagnetic behavior of the complexes. A theoretical fitting of the magnetic data displays higher magnitude of the antiferromagnetic interaction for the terminal dicopper(II) unit in comparison with the central one. Complexes 1 and 2 present a new structural motif involving the pentadentate Schiff base ligand. A significant observation is the non-involvement of the hydroxy group of the carboxylate ligand in covalent bonding. The complexes may be suitable for generation of supramolecular structures involving the pendant OH group of the carboxylate ligands.

### 5. Supplementary material

Variable temperature magnetic susceptibility data for the two complexes (8 pages), crystallographic data for the structures 1.2<sup>i</sup>PrOH and 2 in the CIF format have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC 211826 for 1.2<sup>i</sup>PrOH and 211827 for 2. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-003; e-mail: deposit@ccdc.cam.ac.uk).

# Acknowledgements

Financial support received from the Department of Science and Technology, Government of India, is gratefully acknowledged (SP/S1/F-01/2000). We thank the Bioinformatics Centre of Indian Institute of Science, Bangalore, for database search.

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