μ-η^1:η^1-*N*,*N′*-Imidazolidine-Bridged Dicopper(II/III) Complexes of a New Dinucleating μ-Bis(tetradentate) Schiff Base Ligand: Synthesis, Structural Characterization, ^{1}H NMR Spectroscopy, and Magnetic Coupling

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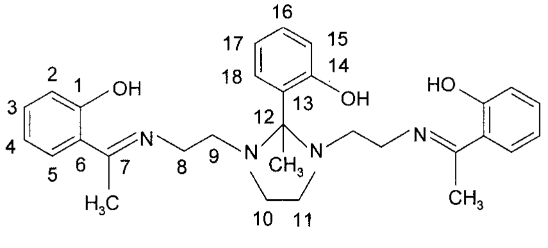
The copper coordination chemistry of a new imidazolidine-based doubly bridging μ-bis(tetradentate) ligand, H_3mhbai is studied. A new family of pentacoordinate dinuclear complexes of formula $[Cu^{II}_2(\mu\text{-mhbai})(\mu\text{-X})]\cdot 2H_2O$ (**1**–**4**) [X = OAc, NO_3, Cl, S_2COMe], where H_3mhbai stands for 2-(2-hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)-4-methyl-3-azabut-3-enyl]-2-methyl-1,3-imidazolidine, were synthesized from the ligand, H_3mhbai in air. The complex **1** was structurally characterized by X-ray crystallography. The μ-η^1:η^1-*N*,*N′*-imidazolidine bridging mode between two copper(II) ions has been identified in this complex along with a nonhelical binding mode of the μ-bis(tetradentate) ligand. Variable temperature (2–300 K) magnetic susceptibility data of **1** show the presence of a weak antiferromagnetic exchange interaction between the two triply bridged magnetically isolated copper(II) ($S = 1/2$) ions. The $\chi_m T$ values start to drop at temperature below 50 K, to reach a value of 0.55 $cm^3 K mol^{-1}$ at 2 K for a coupling constant value of $J = -2.2\ cm^{-1}$. The ^{1}H NMR spectrum of the weakly coupled complex **1** shows a total of seventeen hyperfine shifted peaks, as expected from the idealized C_s symmetry of the compound, spread over a very large window of chemical shift, spanning about 130 ppm.

Introduction

Synthesis and characterization of novel dicopper(II/III) complexes of new diaza heterocyclic bridge[1] incorporated bis(polydentate) ligands is an active area of synthetic inorganic chemistry research during the last couple of years.[2–8] Studies on dicopper complexes of imidazolidine bridging ligands bearing additional chelating side arms in the 1- and 3-positions of the heterocycle are unknown. Dimetal complexes have the potential to provide new reactivity patterns and physical properties that could not be achieved with similar type of mononuclear complexes.[9] It is convenient to classify dinucleating ligands by the number and types of bridging groups that are used to assemble dimetal complexes. For an intimate dimetal complex having small metal–metal separation the maximum number of bridging groups is three. The diaza heterocyclic bridge containing new bis(polydentate) ligands can be developed from the known[10] imidazolidine ring formation reaction on the ethylenediamine segment of the tetramine backbone of the parent hexadentate ligand. This is some kind of chelate elaboration on the potential heterocycle bridge by Schiff base formation using ketones for the first time. Recently we have shown[11] that in absence of the imidazolidine bridging backbone the parent hexadentate ligand can give μ_4-oxo-bridged tetracopper(II) complex through ligand self-assembly. Double helical binding of the hexadentate ligand was also observed there. Dinuclear copper complexes with two metal ions in close proximity have received a great deal of attention in recent times.[12–15] Unlike other potential bridging units such as phthalazine, pyridazine, oxadiazole, thiadiazole, 1,8-naphthyridine,[9] neutral imidazolidine bridge-supported dicopper(II/III) complexes are unknown till date. Here, we report the coordination chemistry of μ-η^1:η^1-*N*,*N′*-imidazolidine-bridged dicopper(II/III) complexes of a new μ-bis(tetradentate) ligand, H_3mhbai {2-(2-hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)-4-methyl-3-azabut-3-enyl]-2-methyl-1,3-imidazolidine} (Scheme 1).



Scheme 1. 2-(2-hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)-4-methyl-3-azabut-3-enyl]-2-methyl-1,3-imidazolidine (H_3mhbai).

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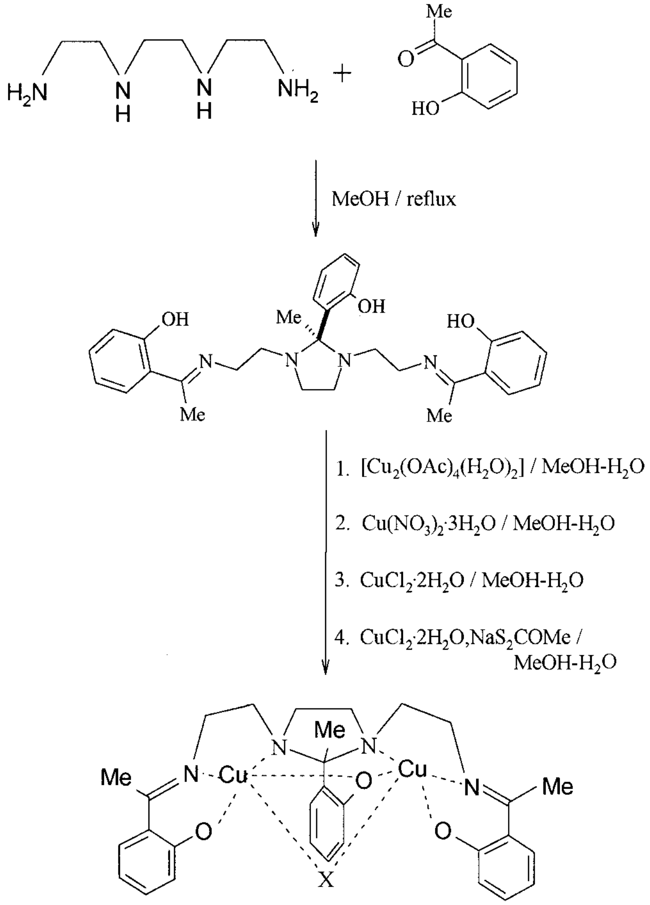
This dinucleating ligand feature a 2-(hydroxyphenyl)-imidazolidine bridge, linking two arms of imine-phenol groups and support dimetallic structures with a variety of exogenous bridging ligands. The complex also binds a water dimer showing a novel example of simple near-linear self-assembled water cluster $(H_2O)_2$ in a crystalline dimetal complex.[16] Recently, it has been discovered that certain imidazole compounds can stabilize similar infinite 1D water chains[17] as potential models of biologically relevant proton wires. Similar tetrameric water structure has also been identified recently in an organic macrocyclic ligand crystal host.[18] The present work also reports the X-ray structural characterization of a dicopper(II/III) complex of a new non-macrocyclic dinucleating ligand satisfying four coordination sites around each copper center and two of which are bridging. From variable temperature magnetic measurement a weak antiferromagnetic (J = –2.2 cm^{-1}) coupling was observed for complex **1** in a distorted square-pyramidal geometry. ^{1}H NMR study of complex **1** also shows that at room temperature the system remains largely paramagnetic due to the very weak nature of the observed antiferromagnetic coupling.

Results and Discussion

Syntheses and Spectroscopic Characterization Studies

The μ-bis(tetradentate) ligand H_3mhbai was synthesized by the known imidazolidine ring formation reaction with 2-hydroxyacetophenone and triethylenetetramine in a mol ratio of 3:1 under reflux for 5 h and isolated in the solid form following a modified Bailer route[19] (Scheme 2). The resulting Schiff base incorporated an imidazolidine ring from the reaction of the third ketone with the two inner adjacent secondary amine nitrogen atoms of trien.[20] The parent hexadentate ligand (H_2bahped) reported earlier[11] producing novel μ_4-oxo-bridged tetracopper(II) was synthesized as a yellow oil from a similar Schiff base condensation reaction of 2-hydroxyacetophenone and triethylenetetramine (trien) in a 2:1 mol ratio under reflux for 0.5 h. In the IR spectrum of the ligand H_3mhbai, the phenolic O–H stretchings of the two terminal rings are observed at 3443 cm^{-1}. The C=N stretching frequency of the ligand is observed at 1616 cm^{-1}. In the EI-MS of the ligand, the molecular ion peak (*m*/*z*) was observed at 500, confirming the formation of the desired imidazolidine ring containing ligand. In ^{1}H NMR spectra the characteristic central methyl protons and terminal methyl protons both appear as singlet at δ = 1.38 and 2.21 ppm, respectively. The characteristic central methyl carbon and terminal methyl carbon atoms appear at δ = 14.51 and 26.58 ppm in ^{13}C NMR spectra, respectively. The imidazolidine ring carbon at the hydroxyphenyl substitution appears at δ = 116.83 ppm. The imine carbon appears at δ = 164.29 ppm. Both ^{1}H and ^{13}C NMR spectroscopic data are comparable with the literature values.[10,21] The signals due to aromatic ring protons were observed in the 6.74–7.40 ppm region. The hydrogen atoms on the imidazolidine backbone appeared as a complex set of overlapping triplet resonance signals at 2.74–2.80 ppm. The reaction of different copper(II) salts with this hitherto unknown ligand in 2:1 molar ratio in alcoholic media at room temperature affords green $[Cu^{II}_2(\mu\text{-mhbai})(\mu\text{-X})]\cdot 2H_2O$ (**1**–**3**) [X = OAc, NO_3, Cl]. Use of a stoichiometric amount of $MeCOS_2^-$ in the reaction of H_3mhbai and $CuCl_2\cdot 2H_2O$ yields $[Cu^{II}_2(\mu\text{-mhbai})(\mu\text{-}S_2COMe)]\cdot 2H_2O$ (**4**) (Scheme 2). They represent a new family of 2-phenolate-substituted imidazolidine-bridged dicopper(II/III) complexes. All the complexes are insoluble in water and separate immediately from the reaction medium. The complexes are soluble in MeCN, DMF and DMSO. The molar conductivity values in DMF are in the range 12 to 29 Ω^{-1}cm^{2}mol^{-1} (28 °C), consistent with the nonelectrolytic formulations of the complexes. The infrared spectrum of the complex **1** shows stretching frequencies at 1586 and 1405 cm^{-1} corresponding to asymmetric and symmetric mode of OAc^- ion present.



Compound	X
1	OAc^-
2	NO_3^-
3	Cl^-
4	$MeOCS_2^-$

Scheme 2.

For complex **2**, the characteristic $\nu_{(N=O)}$ frequencies for bridging NO_3^- group appear at 1378 cm $^{-1}$ and 843 cm^{-1}, respectively, and are similar to the reported values.[22] Complex **4** shows a group of bands between 1021 and 1203 cm^{-1} assigned to ν_{C-O} and ν_{C-S} coupled modes similar to the reported values[23] which are absent in complex **3**. The room temperature magnetic moments per Cu for all the four complexes are in the range of 1.66–1.98 μ_B. Electronic spectra of the complexes **1**–**4** in dimethylformamide solutions show several intense absorption bands in the visible region which are assigned to the allowed d-d and charge transfer transitions. All the complexes exhibit similar type broad bands in 602–627 nm region with molar extinction coefficient of 230–385 L mol^{-1} cm^{-1} for d-d transitions. The higher intensity charge transfer transitions are obtained at 359–370 nm and 268–274 nm range with molar extinction coefficients of 5170–10945 L mol^{-1} cm^{-1} and 15170–24730 L mol^{-1} cm^{-1}, respectively.

X-ray Structure of Cu^{II}_2(μ-mhbai)(μ-OAc)]·2 H_2O

The identity of the compound **1** is established through X-ray structure determination. An ORTEP view of **1** is shown in Figure 1. The selected bond length and bond angles are given in Table 1. Complex **1** consists of a neutral dinuclear [Cu_2(μ-mhbai)(μ-OAc)] molecule with a hydrogen-bonded water dimer. Each copper(II) atom is in a square-pyramidal N_2O_3 environment, made up of one amine nitrogen, one imine nitrogen, one terminal phenol oxygen atom from the dinucleating ligand and one axial acetate oxygen. The exogenous acetate group binds two copper atoms in μ-*syn*-*syn*-η^1:η^1-fashion. The μ-η^1:η^1-*N*,*N′*-imidazolidine and the phenolate groups bridge two copper atoms along the edge of the bi-square-pyramid. Two axial oxygen atoms, from the acetate group, complete the triply bridging motif in the dicopper complex. The μ-bis(tetradentate) ligand connects the copper atoms through μ-η^1:η^1-*N*,*N′*-imidazolidine and phenoxy bridges. The acetate bridging in *syn-syn* bidentate mode is common in diiron and dimanganese complexes[24] and also found in dicopper(II/III) complexes.[25,26] The dinucleating μ-bis(tetradentate) ligand shows a nonhelical binding mode for the dicopper(II/III) complex as against the double helical binding of two parent hexadentate ligands for a tetracopper[(II)$_4$] complex reported recently by us.[11] Two nitrogen atoms, one terminal and one bridging phenolate oxygen atom from one-half of the ligand are coordinated to one metal center forming one five-membered (N–Cu–N) and two six-membered (N–Cu–O) terminal and bridging chelate rings. The chelate bite angle for the five-membered ring is in the range

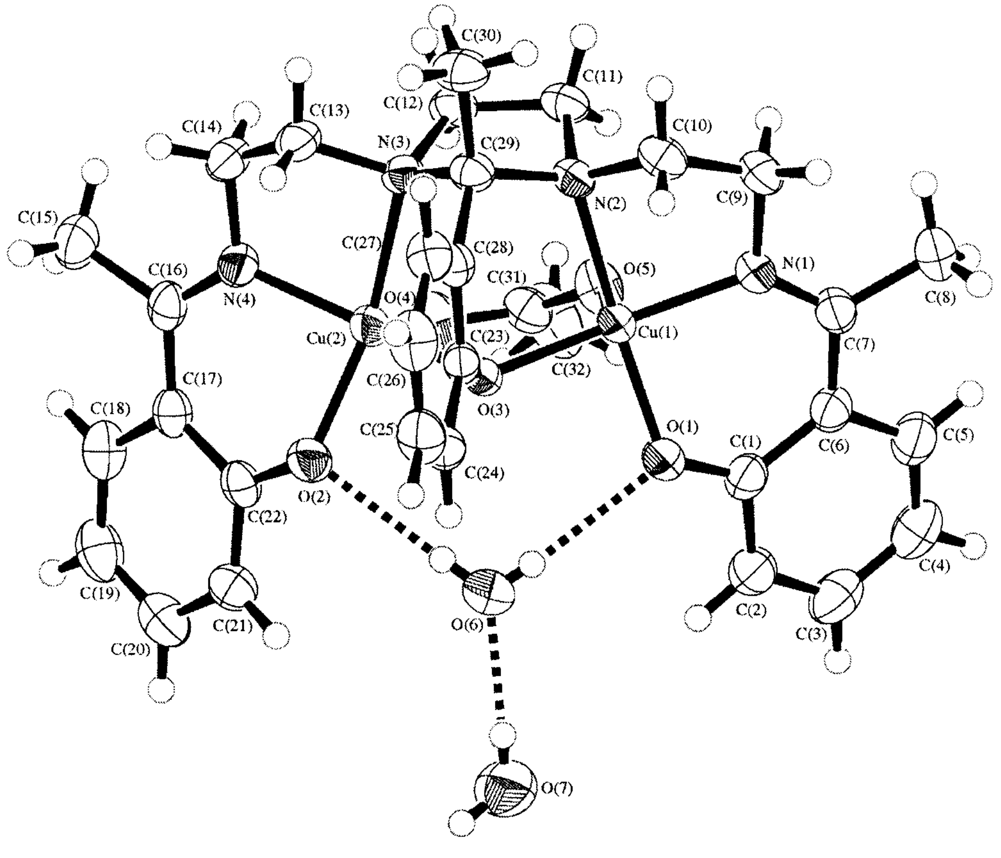


Figure 1. An ORTEP drawing of the neutral molecule [Cu^{II}_2(μ-mhbai)(μ-OAc)]·2 H_2O (**1**) with H bond indicated as dashed lines. Ellipsoids are drawn at 50% probability.

Table 1. Selected bond lengths and angles for $[\mathrm{Cu}^{\mathrm{II}}_2(\mu\text{-mhbai})(\mu\text{-OAc})]\cdot 2\,\mathrm{H_2O}$ (**1**).

Bond lengths [Å]	
Cu(1)–O(1)	1.911(2)
Cu(1)–O(5)	2.190(2)
Cu(1)–N(2)	2.116(2)
Cu(2)–O(3)	1.955(2)
Cu(2)–N(3)	2.203(2)
Cu(1)–O(3)	1.953(1)
Cu(1)–N(1)	1.946(2)
Cu(2)–O(2)	1.934(2)
Cu(2)–O(4)	2.132(2)
Cu(2)–N(4)	1.955(2)
Bond angles [°]	
O(1)–Cu(1)–O(3)	89.70(7)
O(1)–Cu(1)–N(1)	91.66(9)
O(3)–Cu(1)–O(5)	102.64(7)
O(3)–Cu(1)–N(2)	89.98(7)
O(5)–Cu(1)–N(2)	96.80(9)
O(2)–Cu(2)–O(3)	91.29(8)
O(2)–Cu(2)–N(3)	156.85(8)
O(3)–Cu(2)–O(4)	101.46(7)
O(3)–Cu(2)–N(4)	160.18(8)
O(4)–Cu(2)–N(4)	97.90(8)
O(1)–Cu(1)–O(5)	94.60(9)
O(1)–Cu(1)–N(2)	168.38(9)
O(3)–Cu(1)–N(1)	161.74(9)
O(5)–Cu(1)–N(1)	95.39(8)
N(1)–Cu(1)–N(2)	85.07(9)
O(2)–Cu(2)–O(4)	98.34(9)
O(2)–Cu(2)–N(4)	90.07(9)
O(3)–Cu(2)–N(3)	86.70(8)
O(4)–Cu(2)–N(3)	104.67(8)
N(3)–Cu(2)–N(4)	84.33(9)

of 84.33(9)–85.07(9)° and for the six-membered rings it is in the range of 90.07(9)–91.66(9)° for terminal and 86.70(8)–89.98(7)° for bridging. The *cis* angles around the Cu(1) ion range from 85.07(9) to 102.64(7)° with an average value of 93.23° and that around the Cu(2) ion range from 84.33(9) to 104.67(8)° with an average value of 94.34°. The average *trans* angles around Cu(1) ion are 87.38 and 90.82° and that around Cu(2) ion are 87.81 and 88.38°. For acetate coordination the Cu(l)-O(5) distance of 2.190(2) Å differs from the Cu(2)–O(4) distance of 2.132(2) Å by 0.058 Å.

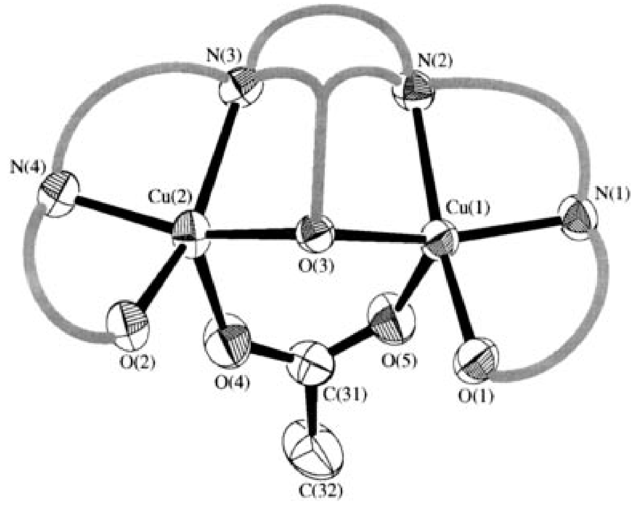


Figure 2. The core of the dinuclear complex $[\mathrm{Cu}^{\mathrm{II}}_2(\mu\text{-mhbai})(\mu\text{-OAc})]\cdot 2\,\mathrm{H_2O}$ (**1**).

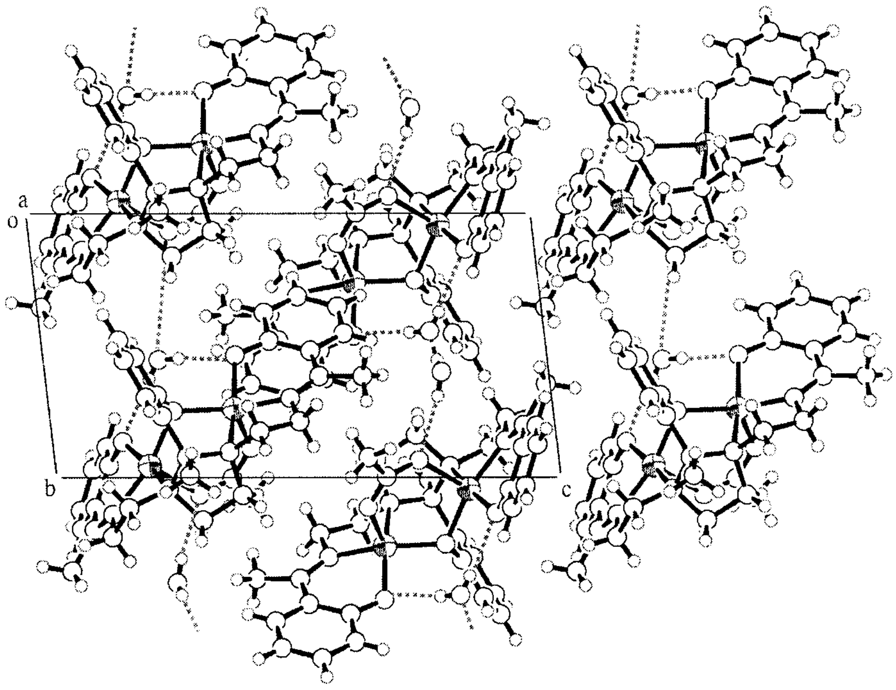


Figure 3. The packing diagram along *b* axis of the neutral molecule $[\mathrm{Cu}^{\mathrm{II}}_2(\mu\text{-mhbai})(\mu\text{-OAc})]\cdot 2\,\mathrm{H_2O}$ (**1**) showing H bonding with water molecules.

This difference in bond length of the two metal ions to the oxygen atoms of the *syn-syn* bidentate carboxylate bridge is usually not larger than 0.10 Å as in other diiron or dimanganese complexes. Endogenous phenolato and exogenous acetato bridging support the formation of the imidazolidine-bridged homodinuclear assembly. The Cu–Cu distance is 3.298(4) Å, which is in the normal range for other triply bridging molecules.[2,27] Longer Cu–N distances [Cu(1)–N(2) = 2.116(2) Å; Cu(2)–N(3) = 2.203(2) Å][28–31] are observed for the tertiary amine nitrogen atoms of the imidazolidine ring to both the copper(II) ions. The Cu–N_{imine} and Cu–O_{phenol} distances are in the normal range. The Cu–O distances for the bridging phenolate coordination indicate that the bridge is practically symmetric [Cu(1)–O(3) = 1.953(1) Å; Cu(2)–O(3) = 1.955(2) Å] for a dicopper complex. Similarly, the Cu(1)–O(5) and Cu(2)–O(4) distances show a high degree of symmetry with respect to the acetate bridge (Figure 2). The complex **1** shows an intricate hydrogen bonding between two water molecules and two terminal phenolic oxygen atoms, attaching a water dimer to the compound. The first water molecule O(6) gives rise intramolecular interactions with both the terminal phenolic oxygen atoms (Figure 1) [O(6)···O(1) = 2.889(3) Å; O(6)···O(2) = 2.931(3) Å]. The hydrogen bonded water molecule provides a pseudo macrocyclic ligand environment around two copper(II) centers. The second water molecule is further hydrogen bonded to the first one [O(7)···O(6) = 2.820(3) Å] and the distance is in between that of liquid water and regular ice (about 2.85 and 2.74 Å).[32] A unit cell packing pattern (Figure 3) is obtained for the complex **1** due to the involvement of the water dimer in the hydrogen bonding network with the complex. Intermolecular hydrogen bonding is operative between the second water molecule O(7) and one of the acetate oxygen atom of another dicopper molecule.

Magnetochemistry of Cu^{II}_2(μ-mhbai)(μ-OAc)]·2 H_2O

The degree of magnetic superexchange interaction within the dinuclear complex [Cu^{II}_2(μ-mhbai)(μ-OAc)]·2 H_2O (**1**) was evaluated by means of variable temperature bulk magnetic susceptibility measurements in the 2–300 K temperature range, under a constant magnetic field of 0.8 T. The results are presented in Figure 4 in a form of $\chi_m T$ vs. T plot, where χ_m is the molar magnetic susceptibility after correction for the diamagnetic contribution and that of temperature independent paramagnetism (which were combined in one unique parameter). In this plot, $\chi_m T$ remains almost constant over most of the temperature range, at its 300 K value of 0.88 $cm^3 K mol^{-1}$, consistent with two magnetically isolated Cu^{II} ($S = 1/2$) centers in the molecule. The product $\chi_m T$ starts drop at temperatures below 50 K, to reach a value of 0.55 $cm^3 K mol^{-1}$ at 2 K. These results indicate that the coupling between Cu^{II} ions within **1** is very weak and antiferromagnetic in nature. A quantitative description of this behavior was performed by fitting the experimental data to a theoretical model using the Bleaney–Bowers equation[33,34] as the expression for $\chi_m = f(T)$. The convention employed for the phenomenological description of the magnetic coupling is conveyed by the Heisenberg-Spin Hamiltonian $\boldsymbol{H} = -2\boldsymbol{J}\boldsymbol{S}_1\boldsymbol{S}_2$. Satisfactory fits could only be obtained when the data at lowest temperatures were excluded. This is presumably because at such temperatures, weaker effects begin to surface, which are not included in the model, such as intermolecular interactions. Thus, a least-squares procedure was carried out to model the data above 8 K. The best fit (Figure 4, solid line) ensued from $J = -2.2\ cm^{-1}$ and $g = 2.17$. The magnetic superexchange in dinuclear systems such as complex **1** has been explained in numerous previous examples in terms of the overlap between the magnetic orbitals of the Cu^{II} ions through the intermediacy of the bridging ligands.[35] In complex **1**, the metal ions are in a distorted square-pyramidal geometry, the apical positions being occupied by the oxygen atoms from the μ–AcO^- bridge. Therefore, the magnetic orbitals are $d_{x^2-y^2}$ and can only interact via the phenol bridging moiety. A magneto-structural study has established the correlation existing between the Cu–O–Cu angle and J in bis(phenoxide)-bridged [Cu_2] complexes, and has shown the strong antiferromagnetic character of this coupling.[36] In the mentioned study, both μ-phenoxide groups occupy equatorial coordination positions from Cu^{II}, thereby providing for two strong exchange pathways. Complex **1** however, belongs to the smaller group of compounds displaying one phenoxide and one η^1:η^1:μ_2-acetate bridge. In this family, the magnetic coupling has been found to be much weaker[37–39] and in very few exceptions a ferromagnetic type of exchange has been claimed.[40] This is consistent with the fact that in these compounds there is only one possible pathway for the exchange. In addition, it has been argued that the angle between the equatorial planes around Cu^{II} exerts a significant influence on the magnitude of J.[41] In particular, a deviation of this angle from zero degrees causes the decrease of the energy gap between the symmetric (φ_s) and the antisymmetric (φ_a) combination of magnetic orbitals, diminishing the antiferromagnetic nature of the coupling. In compound **1**, the idealized Cu^{II} equatorial planes are significantly bent, forming an angle 38.32°, to which

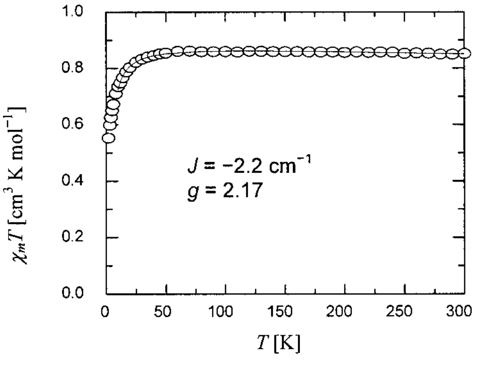


Figure 4. Plot of $\chi_m T$ vs. T per mol of complex [Cu^{II}_2(μ-mhbai)(μ-OAc)]·2 H_2O (**1**). Data have been corrected for sample diamagnetic contributions and temperature independent paramagnetism. The solid line is the best fit to the experimental data above 8 K (see text for details).

could be ascribed the small value of J calculated above. Comparisons of complex **1** with previous systems, however, are thwarted by the unique structural features imposed on this assembly by the dinucleating ligand. This is perhaps most evident in the unconventional orientation of the C–O bond of the bridging phenoxide with respect to the plane containing the Cu–O–Cu atoms from that bridge. Useful for this discussion could be the suggestion that μ-acetates and alkoxide bridges, when simultaneously present in this type of [Cu_2] complexes, are *counter-complementary*, leading to a reduction of the $\varphi_s - \varphi_a$ energy gap and therefore, of the absolute value of J.[42] In the present case however, this mechanism can not operate because the AcO^- group is bound to the axial positions of Cu^{II} and, therefore, is not interacting with the magnetic orbitals of the metals.

EPR Spectroscopy of Cu^{II}_2(μ-mhbai)(μ-OAc)]·2 H_2O

Powder X-Band (9.7857 GHz) EPR spectra were collected for complex **1** at room temperature and 77 K. The latter one is shown in Figure 5. In both the cases, the obtained spectra could be interpreted in terms of mononuclear Cu^{II} chromophores in a *quasi* axial geometry, which is in line with the above revelation that at these temperatures, the ions within the complex are essentially uncoupled. Thus, consistent with the asymmetric square-pyramidal geometry of the metal centers in **1**, with a *cis*-N_2O_2 equatorial donor set, three components of g can be observed, with $g = 2.17$ and $g_\perp$ split in two; $g_x = 2.12$ and $g_y = 2.07$. The lower field side of the parallel signal shows a shoulder that could be interpreted as the manifestation of small hyperfine splitting of this signal as a result of the coupling with the nuclear spin from $^{3/2}$Cu. The average isotropic g-factor resulting from these measured values is $g = 2.12$, which is in reasonable agreement with the value calculated from fitting the bulk magnetization measurements (see above).

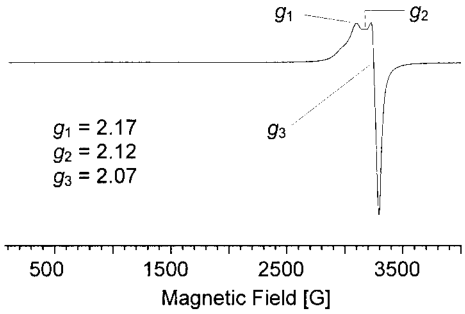


Figure 5. Powder X-band EPR spectrum of complex [Cu^{II}_2(μ-mhbai)(μ-OAc)]·2 H_2O (**1**) at ca 77 K.

^1H NMR Spectroscopy of Cu^{II}_2(μ-mhbai)(μ-OAc)]·2 H_2O

^1H NMR spectroscopy has been shown to be applicable to characterization of the structure and reactivity of dicopper(II/II) complexes with magnetic coupling that ranges from weakly ferromagnetic to strongly antiferromagnetic.[43] Few reports have described copper(II) complexes that produce narrow ^1H NMR resonances.[44–49] Paramagnetic NMR of dinuclear copper complexes has been used extensively in order to establish their relevance as models for metal sites in copper enzymes.[50] Construction of a library of compounds along with their NMR properties is beneficial in the context of bioinorganic modeling of naturally occurring metallo-enzymes. 250-MHz ^1H NMR spectroscopic data of complex **1** were collected in [D_4]methanol at room temperature. The T_1 value of almost every observed resonance has been determined for helping in the assignment of the spectrum. For this, it was taken into consideration that the relaxation time T_1 of protons within paramagnetic complexes is proportional to r^{-6}, where r is the distance from the observed H nucleus to the metallic center. The T_1 values and the chemical shifts, δ, of all resonances are collected in Table 2, whereas the spectrum with the assignment of the signals are shown in Figure 6. Complex **1** is only scarcely soluble in MeOH, therefore, a large number of scans needed to be collected before an acceptable signal-to-noise ratio could be attained. The spectrum of **1** shows a total of seventeen hyperfine shifted peaks, as expected from the idealized C_s symmetry of the compound, spread over a very large window of chemical shift, spanning about 130 ppm. This reflects the fact that at room temperature the system remains largely paramagnetic as a result of the very weak nature of the observed antiferromagnetic coupling. In addition, peaks attributed to MeOH and free ligand were detected. The assignment of the latter peaks was made on the basis of their smaller relative intensity with respect to the rest of the signals. The signals from the solvent were used as internal reference. Inspection of the intensity integrals of these seventeen resonances allowed their grouping into four sets of one (a), two (b), ten (c), and four (d) signals, respectively, integrating for six, three, two and one proton, as predicted from the structure of **1** (Figure 6, top). These groups correspond to the following categories of protons: Group "a", only one signal, which integrates for six protons, corresponding to the two equivalent methyl groups in α to the imine N atoms, and which was readily assigned; group "b", two signals with intensities equivalent to three protons each, arising from two inequivalent methyl groups, respectively. These correspond to the μ-acetate and to the methyl attached to the central five-membered ring of the ligand. The assignment of these two signals to either of both groups remains ambiguous since the distances of the protons to the Cu^{II} ions is very similar in both cases; group "c" is the most numerous. It includes ten signals with intensity ratios for two H nuclei. These result from the hydrogen atoms attached to the amine groups (six signals) and from those attached to the two external phenyl rings (which are equivalent). The peaks from the first sub-group are broader than these of the second, since the protons causing the former are crystallographically closer to the metal centers. Again, the assignment could be made almost unambiguously on the basis of the T_1 values. Where T_1 was so small that could not be measured, the broadness of the peaks was used as an approximate measure of the relative relaxation times. The resonances of the other sub-group are sharper and show the alternation of chemical shifts characteristic of π-delocalization mechanisms.[51] This, along with relaxation time data helped in the assignment of the resonances; group "d" is the last set of signals, which includes the four peaks from the central phenyl ring of the ligand (one proton per signal). Here is also evident a mechanism of π-delocalization of the electronic spin, which was useful in the assignment of the peaks. With this study, complex **1** enters the small group of binuclear [Cu_2] complexes of which, the ^{1}H NMR spectrum could be explained almost unambiguously and is a valuable contribution to the growing body of spectroscopic data which can be useful in the functional and structural study of the metallo-enzymes.

Table 2. ^{1}H NMR data of [Cu^{II}_2(μ-mhbai)(μ-OAc)]·2 H_2O (**1**).

Signal	δ [ppm]	T_1 [ms]	Signal	δ [ppm]	T_1 [ms]
a	–12.7	20	c_7	16.6	31
b_1	38.1	49	c_8	5.2	t.s.[a]
b_2	10.7	8.2	c_9	1.3	t.s.[a]
c_1	184	t.f.[b]	c_{10}	–10.8	7.5
c_2	123	t.f.[b]	d_1	33.4	26
c_3	122	t.f.[b]	d_2	17.7	17
c_4	91	4.5	d_3	–20.5	21
c_5	78	5.0	d_4	–26.6	t.f.[b]
c_6	28	2			

[a] Too slow to be measured within the time scale of the experiment. [b] Too fast to be measured within the time scale of the experiment.

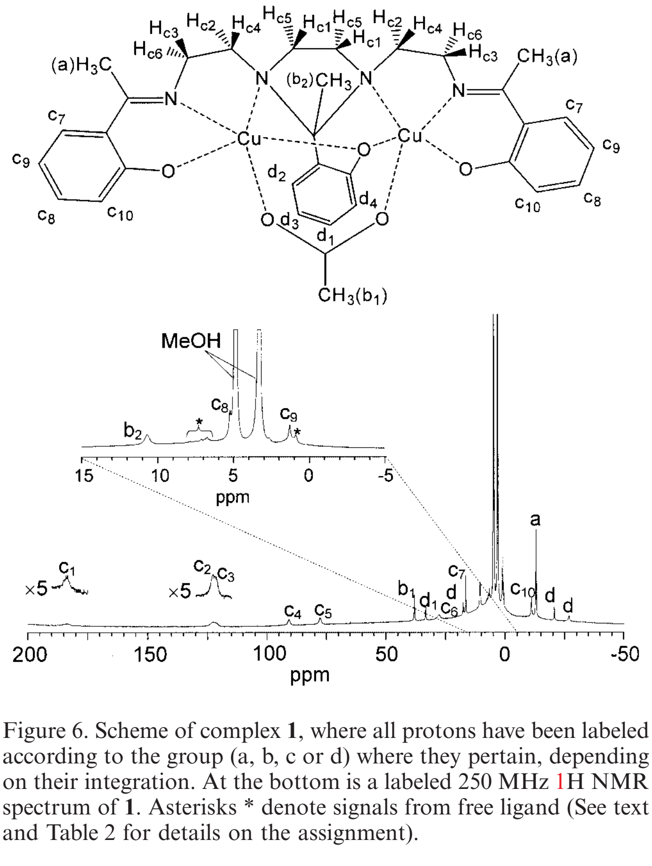


Figure 6. Scheme of complex **1**, where all protons have been labeled according to the group (a, b, c or d) where they pertain, depending on their integration. At the bottom is a labeled 250 MHz 1H NMR spectrum of **1**. Asterisks * denote signals from free ligand (See text and Table 2 for details on the assignment).

Electrochemistry of [Cu^{II}_2(μ-mhbai)(μ-S_2COMe)]·2 H_2O

The electron-transfer behaviour of the complex [Cu^{II}_2(μ-mhbai)(μ-S_2COMe)]·2 H_2O (**4**) in dimethylformamide has been studied by cyclic voltammetry. A glassy-carbon working electrode with tetraethylammonium perchlorate (TEAP) as supporting electrolyte at 298 K were used. The cyclic voltammogram was recorded in the potential range of 0.0 to +0.9 V vs. saturated calomel electrode (SCE) at a scan rate of 50 mV s^{-1}. Complexes **1**–**3** do not display any characteristic cyclic voltammetric response within the above-mentioned potential window. Only the xanthate-bridged complex **4** exhibits a quasi-reversible response at $E_{1/2}$ = 0.504 V (ΔE_p = 132 mV). The observed quasi-reversible peak is assigned to an one electron transfer process [Equation (1) for ligand oxidation.The ligand centered oxidation is known in several sulfur-based ligand systems where thiyl radical formation is predicted for an instance when ligand-based oxidation occurs rather than metal-based.[52]

$$[Cu^{II}\{\mu\text{-MeO(C=S)S}^-\}Cu^{II}]^{3+} - e^- \leftrightarrow$$
$$[Cu^{II}\{\mu\text{-MeO(C=S)S}^{\cdot}\}Cu^{II}]^{4+} + e^- \qquad (1)$$

The quasi-reversible nature of the voltammogram indicate the formation of a methoxythiyl radical coordinated to a metal ion with a weak Cu–$^{\cdot}$S(C=S)OMe bond. The absence of any voltammetric response in analogous acetate-bridged complex (**1**) also shows the easy oxidizing nature of thio derivatives.[52] At 298 K the oxidized species is stable at the voltammetric time-scale only.

Concluding Remarks

The results presented here demonstrate the synthesis, structural characterization and magnetic behaviour of imidazolidine-bridged Cu^{II}–Cu^{II} triply-bridged intimate complex supported by a new μ-bis(tetradentate) Schiff-base ligand. Complex **1** is the example of a new structurally characterized μ-η^1:η^1-*N*,*N'*-imidazolidine-bridged dicopper(II/III) complex. Neither triply-bridged structure nor the imidazolidine bridge is responsible for any strong magnetic interaction. Two copper(II) ions at a distance of 3.2984 Å show only a weak magnetic interaction. The isolated new dicopper(II/III) complexes have [Cu_2(μ-imidazolidine)]$^{4+}$ core and currently we are engaged in synthesizing analogues complexes of other 3d and 4d metal ions to explore the role of bridging imidazolidine moiety in the molecular structure and physical properties of new complexes.

Experimental Section

Materials and Physical Measurements: The chemicals used were obtained from the following sources: Triethylenetetramine and carbon disulfide from S.D. Fine Chem, India. 2-Hydroxyacetophenone from Spectrochem, Mumbai, India. Cupric acetate hydrate and cupric chloride dihydrate from SRL, India. Cupric nitrate trihydrate from E. Merck, India. All other chemicals and solvents were reagent grade materials and were used as received without further purification. The elemental analyses (C, H, N) were performed with a Perkin–Elmer model 240 C elemental analyzer. ^1H and ^{13}C NMR spectra of the ligand were obtained with a Bruker AC 200 NMR spectrometer using TMS as the internal standard. ^1H NMR spectra of the complex were collected with a 250 MHz Bruker DXR 250 spectrometer. Longitudinal relaxation times (T_1) were measured using an inversion-recovery pulse sequence (180-τ-90°) with a 300 MHz Varian Unity-300 spectrometer. In all cases, the protiosolvent signal was used as reference and chemical shifts were quoted on the δ scale (down field shifts are positive). IR spectra were recorded with a Perkin–Elmer 883 spectrophotometer. The solution electrical conductivity and electronic spectra were obtained with a Unitech type U131C digital conductivity meter with a solute concentration of about 10^{-3} M and a Shimadzu UV 3100 UV/Vis-NIR spectrophotometer, respectively. Mass spectra were obtained with a Finnigan MAT 8200 (electron ionization, EIMS) instrument. The room temperature magnetic susceptibilities in the solid state were measured using a home built Gouy balance fitted with a polytronic d.c. power supply. The experimental magnetic susceptibilities were corrected for the diamagnetic response using Pascal's constants.[53] Magnetic measurements were carried out at the "Servei de Magnetoquímica (Universitat de Barcelona)" on polycrystalline samples (ca. 40 mg) by using a Quantum Design MPMS XL-5 SQUID susceptometer operating at a constant magnetic field of 0.8 T between 2 and 300 K. The experimental magnetic moment was corrected for the diamagnetic contribution from the sample holder. X-Band EPR measurements (9.7857 GHz) were performed at room temperature and ca. 77 K on powdered samples a Bruker Spectrometer (ESR, 300E), working with an oxford helium liquid cryostat for variable temperature. Electrochemical measurements were made using a PAR model 173 potentiostat/galvanostat, 175 universal programmer, 178 electrometer, and 377-cell system. A glassy carbon working-electrode, a platinum-wire auxiliary-electrode, and an aqueous saturated calomel reference electrode (SCE) were used in a three-electrode configuration. A digital series 2000 Omni Graphic recorder was used to trace the voltammograms. Electrochemical measurements were made under nitrogen.

Synthesis of 2-(2-Hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)-4-methyl-3-azabut-3-enyl]-2-methyl-1,3-imidazolidine (H_3mhbai): A solution of triethylenetetramine (3.7 g, 25.3 mmol) in methanol (25 mL) was added dropwise to a methanolic solution (25 mL) of 2-hydroxyacetophenone (10.2 g, 74.9 mmol) with stirring at room temperature. The yellow solution was then refluxed for 5 h. The solvent was evaporated in air. The yellow solid was separated by filtration through G4 sintered bed and washed thoroughly with hexane and water. Finally the isolated compound was dried in vacuo with P_4O_{10}. Yield 9.3 g (75%), m.p. 184–186 °C. $C_{30}H_{36}N_4O_3$ (500.6): calcd. C 71.97, H 7.25, N 11.19; found C 71.51, H 7.62, N 11.49. Mass spectrum (EI): *m/z* 500 ($M^+ = L^+$). IR (cm^{-1}, KBr disk): $\tilde{\nu}$ = 3443 [w, ν(phenolic OH)], 1616 [s, ν(C=N)], 1371 [s, ν(phenolic C–O)], 835 [m, ν(CH_2)], 745 [m, ν(aromatic CH)]. ^1H NMR ($CDCl_3$, ppm): δ = 16.13 (s, 2 H, terminal phenolic OH), 12.03 (s, 1 H, pendant phenolic OH), 7.21–7.48 (m, 8 H, H^{2-5}), 6.74–6.89 (m, 4 H, H^{15-18}), 3.47–3.55 (m, 4 H, H^8), 2.86 (t, 4 H, H^9), 2.74–2.80 (m, 4 H, H^{10} and H^{11}), 2.21 (s, 6 H, $H_{\text{terminal methyl}}$), 1.138 (s, 3 H, $H_{\text{central methyl}}$). ^{13}C NMR ($CDCl_3$, ppm): δ = 164.29 (C^7), 162.38 ($C^{1,14}$), 132.48 (C^6), 130.68 ($C^{16,18}$), 128.00 ($C^{3,5}$), 119.18 (C^{17}), 118.88 (C^4), 118.39($C^{2,15}$), 116.83 (C^{12}), 49.61 (C^8), 49.44 (C^9), 49.10 (C^{10}), 26.58 ($C_{\text{terminal methyl}}$), 14.51 ($C_{\text{central methyl}}$).

Synthesis of the Complexes: A general procedure was followed for the preparation and isolation of all complexes of type [Cu^{II}_2(μ-mhbai)(μ-X)]·2 H_2O. Details are given below for the representative cases.

[Cu^{II}_2(μ-mhbai)(μ-OAc)]·2 H_2O (1): An aqueous solution (10 mL) of $Cu(OAc)_2$·H_2O (0.399 g, 1.9 mmol) was slowly added dropwise at ambient temperature to a magnetically stirred warm methanolic solution (15 mL) of H_3L (0.5 g, 0.9 mmol) during a period of 15 min. After complete addition a dark green compound was seen separating in solution. The whole reaction mixture was stirred for 1 h at room temperature. The solvent was evaporated in air. The green precipitate was filtered through a glass frit and washed with water followed by ethanol and hexane and finally dried in vacuo over P_4O_{10}. Yield: 0.61 g (85%). $C_{32}H_{40}Cu_2N_4O_7$ (719.8): calcd. C 53.40, H 5.60, N 7.78, Cu 17.65; found C 52.91, H 5.36, N 7.37, Cu 17.90. IR (cm^{-1}, KBr disk): $\tilde{\nu}$ = 3415 (b), 1605 (vs), 1586 (s), 1532 (s), 1405 (s), 1312 (s), 1201 (s), 869 (s), 755 (s). Molar conductance, Λ_M: (DMF) = 16.36 ohm^{-1}cm^{2}mol^{-1}. UV/Vis (DMF): λ_{max} (ε, L mol^{-1}cm^{-1}) = 616 (385), 368 (10945), 300 (11780) sh, 273 nm (24730). μ_{eff} (tot.): 2.43 μ_B; μ_{eff}/Cu: 1.71 μ_B.

[Cu^{II}_2(μ-mhbai)(μ-NO_3)]·2 H_2O (2): This compound was prepared following the above procedure using $Cu(NO_3)_2$·3 H_2O and triethylamine. The stirring was continued for 1 h. Yield: 0.54 g (75%). $C_{30}H_{37}Cu_2N_5O_8$ (722.7): calcd. C 49.85, H 5.16, N 9.69, Cu 17.58; found C 49.51, H 4.96, N 9.37, Cu 17.01. IR (cm^{-1}, KBr disk): $\tilde{\nu}$ = 3438 (b), 1611 (vs), 1588 (s), 1539 (s), 1453 (s), 1403 (s), 1378 (s), 1297 (s), 1201 (s), 824 (s), 735 (s). Molar conductance, Λ_M: (DMF) = 12.48 ohm^{-1}cm^{2}mol^{-1}. UV/Vis (DMF): λ_{max} (ε, L mol^{-1}cm^{-1})] = 602 (230), 361 (7045), 268 nm (16505). μ_{eff} (tot.): 2.35 μ_B; μ_{eff}/Cu: 1.66 μ_B.

[Cu^{II}_2(μ-mhbai)(μ-Cl)]·2 H_2O (3): This compound was prepared following the above procedure using $CuCl_2$·2 H_2O. The stirring was continued for 1 h. Yield: 0.56 g (80%). $C_{30}H_{37}ClCu_2N_4O_5$ (696.2): calcd. C 51.76, H 5.36, N 8.05, Cu 19.24; found C 51.33, H 5.67, N 8.34, Cu 19.18. IR (cm^{-1}, KBr disk): $\tilde{\nu}$ = 3396 (b), 1602 (vs), 1530 (s), 1319 (s), 1277 (s), 891 (s), 734 (s). Molar conductance, Λ_M: (DMF) = 29.26 ohm^{-1}cm^{2}mol^{-1}. UV/Vis(DMF): λ_{max} (ε, L mol^{-1}cm^{-1}) = 623 (110), 359 (5170), 272 nm (15170). μ_{eff} (tot.): 2.81 μ_B; μ_{eff}/Cu: 1.98 μ_B.

[Cu^{II}_2(μ-mhbai)(μ-S_2COMe)]·2 H_2O (4): This compound was prepared following the above procedure, using $CuCl_2$·2 H_2O and NaS_2COMe. The stirring was continued for 1 h. Yield: 0.59 g (77%). $C_{32}H_{40}Cu_2N_4O_6S_2$ (767.9): calcd. C 50.05, H 5.25, N 7.29, Cu 16.55; found C 50.41, H 4.96, N 7.81, Cu 16.62. IR (cm^{-1}, KBr disk): $\tilde{\nu}$ = 3410 (b), 1607 (vs), 1527 (s), 1318 (s), 1203 (s), 1144 (s), 1021 (s), 861 (s), 724 (s). Molar conductance, Λ_M: (DMF) = 20.18 ohm^{-1}cm^{2}mol^{-1}. UV/Vis (DMF): λ_{max} (ε, L mol^{-1}cm^{-1}) = 627 (225), 370 (8350), 315 (10380), 274 nm (19225). μ_{eff} (tot.): 2.68 μ_B; μ_{eff}/Cu: 1.89 μ_B.

X-ray Crystallographic Procedures for [Cu^{II}_2(μ-mhbai)(μ-OAc)]·2 H_2O (1): The green plate-like single crystals of complex [Cu^{II}_2(μ-mhbai)(μ-OAc)]·2 H_2O suitable for the X-ray analysis were grown by the slow evaporation of a acetonitrile/water solution of the complex. The intensity data of the complex were collected on Bruker SMART CCD X-ray diffractometer using a single crystal with dimensions $0.01 \times 0.22 \times 0.25$ mm^3 that uses graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) by ω-scan method. Precise unit cell dimensions were determined by least-squares refinement of 25 strong reflections having 2θ values. Data were collected at 298 K. A total of 7019 reflections were recorded with Miller indices $h_{min} = 0$, $h_{max} = 11$, $k_{min} = -14$, $k_{max} = 14$, $l_{min} = -21$, $l_{max} = 21$. In the final cycles of full-matrix least-squares on F^2 all non-hydrogen atoms were assigned anisotropic thermal parameters and refinement converged at $R = 0.034$. The residual electron density is in the range +0.73 to –0.64 e·Å^{-3}. The positions of the H atoms bonded to C atoms were calculated (C–H distance

0.96 Å). The structure was solved on a PC 486 by using the DIRDIF92-PATTY programme system[54] and refined by full-matrix least-squares methods with use of the programme SHELX-97[55]/TEXSAN.[56] Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[57] Information concerning X-ray data collection and structure refinement of the compound is summarized in Table 3.

Table 3. Crystallographic data for compound $[Cu^{II}_2(\mu\text{-mhbai})(\mu\text{-OAc})]\cdot 2H_2O$ (**1**).

Emoirical formula	$C_{32}H_{40}Cu_2N_4O_7$
Molecular mass	719.78
Crystal system	triclinic
Space group	*P*-1(2)
a [Å]	8.879(1)
b [Å]	11.329(2)
c [Å]	16.412(2)
α [°]	99.40(1)
β [°]	93.57(1)
γ [°]	107.520(1)
V [Å^3]	1542.2(4)
$D_{\text{calcd.}}$ [g cm^{-3}]	1.550
Z	2
$F(000)$	748.00
Λ [Å]	0.71073
T [K]	298(1)
Crystal size [mm]	0.01 × 0.22 × 0.25
μ [mm^{-1}]	1.434
R[a], R_w [$I > 2\sigma(I)$][b]	0.034, 0.040
GOF	1.043
Final difference map	
Max./min. resid. electron density [e·Å^{-3}]	0.73/–0.64

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$. $w = 0.75/(\sigma^2(F_o) + 0.0010F_o^2)$.

CCDC-259334 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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