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A Combined Experimental and Theoretical Study on the Magnetic Properties of a Family of Bis(μ-phenoxido)dicopper(II) Complexes Bearing ω-[Bis(2-hydroxy-3,5-dimethylbenzyl)amino]alkan-1-ol Ligands

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Five new neutral bis(μ-phenoxido)dicopper(II) complexes, $[Cu_2(\mu\text{-}HL1)_2]\cdot 3EtOH\cdot H_2O$ (**1**), $[Cu_2(\mu\text{-}HL2)_2]\cdot 1.65H_2O$ (**2**), $[Cu_2(\mu\text{-}HL3)_2(\mu\text{-}H_2O)]$ (**3**), $[Cu_2(\mu\text{-}HL4)_2]$ (**4**) and $[Cu_2(\mu\text{-}HL5)_2(\mu\text{-}H_2O)]$ (**5**), were prepared from a family of ω-[bis(2-hydroxy-3,5-dimethylbenzyl)amino]alkan-1-ol ligands (H_3L1–H_3L5 derived from 2-aminoethanol, 3-aminopropanol, 4-aminobutanol, 5-aminopentanol and 6-aminohexanol, respectively) bearing a [O,N,O,O′] donor set. In complexes **3** and **5**, there is also a bridging water molecule between the metallic centres. The copper(II) coordination planes of all these complexes form a roof-like structure (the bridging O atoms are located at the top of the roof). The structural differences found for the different complexes and their relation with the magnetic properties is discussed below. Magnetic studies of these dinuclear complexes showed that *J* values vary from –470.8 to –91.2 as the Cu–O–Cu angles (θ) vary from 100.66(9) to 92.76(7)°. DFT theoretical calculations produced the corresponding magnetic exchange coupling constants, finding that these values are quite near to the experimental ones. A linear relationship between the calculated *J* values and θ was observed, clearly supporting that the major factor controlling the magnetic exchange coupling in this series of complexes is, by far, the Cu–O–Cu bridging angle. The crossover point below which the magnetic behaviour changes from antiferromagnetic to ferromagnetic coupling is predicted at ≈ 89°.

Introduction

Dinuclear copper(II) complexes involving a Cu_2O_2 bridging unit have played a significant role in fields such as copper(II) containing enzymes and molecular magnetism.[1] Bis(μ-hydroxido)- and bis(μ-alkoxido)dicopper(II) complexes have been extensively studied from a magnetostructural point of view. Experimental and theoretical results have revealed that there exists linear correlations between the Cu–O–Cu angle (θ) and the magnetic coupling constant (*J*) for these complexes with planar Cu_2O_2 entities (hydroxide and alkoxide groups bridge metal ions in an equatorial–equatorial fashion).[2,3] The antiferromagnetic (AF) interaction decreases with a decrease in the θ angle, showing a crossover point [below which the magnetic behaviour changes from AF to ferromagnetic (F) coupling with $J = 0$] at about 97°. It was also shown that the position of the crossover point depends on the τ angle (out-of-plane displacement of the hydrogen or carbon atoms linked to the oxygen bridging atoms from the Cu_2O_2 plane), so that the AF coupling decreases with an increase in the τ angle.[4] As expected, when either the core Cu_2O_2 plane is folded or the oxygen atoms bridge metal ions in an equatorial–axial fashion, the observed *J* values significantly deviate from those predicted by the linear correlations. A similar linear correlation between θ and the coupling constant *J* was proposed for bis(μ-phenoxido)dicopper(II) macrocyclic complexes, the crossover point being as low as ≈77°.[5] In view of the results found for hydroxido- and alkoxido-bridged dicopper(II) complexes, this θ value seems to be too low. Numerous examples of structurally and magnetically related bis(μ-phenoxido)dicopper(II) complexes exist, and with the exception of a few cases, they all exhibit moderate to strong AF coupling.[6] In spite of the great body of experimental results for these complexes, there is not yet a clear understanding of the structural parameters controlling the magnetic exchange process and which of them are the most important. To this end, it would be very valuable to dispose of a family of closely related bis(μ-phenoxido)dicopper(II) structures. In this context, we report here the syntheses, crystal structure and magnetic study (theoretic and experimental) of five bis(μ_2-phenoxido)dicopper neutral complexes, $[Cu_2(\mu\text{-}HL1)_2]\cdot 3EtOH\cdot H_2O$ (**1**), $[Cu_2(\mu\text{-}HL2)_2]\cdot 1.65H_2O$ (**2**), $[Cu_2(\mu\text{-}HL3)_2(\mu\text{-}H_2O)]$ (**3**), $[Cu_2(\mu\text{-}HL4)_2]$ (**4**)

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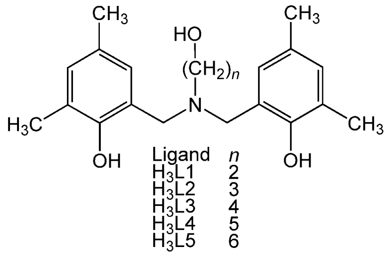
and [Cu_2(μ-HL5)$_2$(μ-H_2O)] (**5**), which were prepared from a family of ω-[bis(2-hydroxy-3,5-dimethylbenzyl)amino]alkan-1-ol ligands (Scheme 1). The increase in the number of carbon atoms in the backbone of the aminoalkyl chain on going from **1** to **5** led us to expect a change in the copper coordination environment and, consequently, to a change in its geometry; the structural features of the Cu_2O_2 bridging unit were also expected to be altered.



Scheme 1. The ω-[bis(2-hydroxy-3,5-dimethylbenzyl)amino]alkan-1-ol ligands.

Results and Discussion

The preparation of the ω-[bis(2-hydroxy-3,5-dimethylbenzyl)amino]alkan-1-ol ligands was accomplished through a Mannich reaction of 2,4-dimethylphenol, paraformaldehyde and the corresponding amino alcohol in 2:1:1 molar ratio. The ligands, after deprotonation of the phenol groups with triethylamine, react with $Cu(NO_3)_2·3H_2O$ in ethanol in a 1:1 molar ratio to afford in good yields the neutral dinuclear copper complexes **1**–**5**. The syntheses can be done straightforwardly and in good yields, if a certain amount of water is present in the ethanolic reaction solution. Details can be found in the Experimental Section. The complexes are very soluble in organic solvents such as $CHCl_3$, EtOH and MeOH. The good solubility in $CHCl_3$ reveals that the complexes are neutral units in organic noncoordinating solvents.

Structural Studies of the Complexes

Crystal Structure of [$Cu_2(HL1)_2$]·3EtOH·H_2O (1)

This complex crystallizes in the monoclinic space group with an asymmetric binuclear Cu_2-(μ-OPh)$_2$ rectangular core (Figure 1a). The relevant bonding parameters for complex **1** are presented in Table 1. The H_3L1 ligand coordinates as a $HL1^{2-}$ anion (both phenol groups are deprotonated) in a tetradentate/bridging manner through the two phenolate oxygen atoms and the oxygen and nitrogen atoms of the amino alcohol group. Each copper(II) ion exhibits a slightly distorted square-pyramidal $CuNO_4$ coordination environment (see δ parameter in Table 3). In this description the bridging and nonbridging phenolate oxygen atoms of the same ligand and the amine nitrogen and the bridging phenolate oxygen atoms of the neighbouring ligand occupy the basal positions with Cu–O bond lengths close to 2 Å, whereas the oxygen atom of the alcohol group occupies the apical position at a longer distance. The coordination planes around Cu1 (atoms Cu1, O1, N8, O2, O4) and Cu2 (atoms Cu2, O4, N38, O5, O1) form a folded geometry with a roof angle of 44.3(6)°. The oxygen atoms of the nonbridging phenolate groups, the water molecules and the ethanol molecules are involved in hydrogen-bonding interactions (Figure 1b).

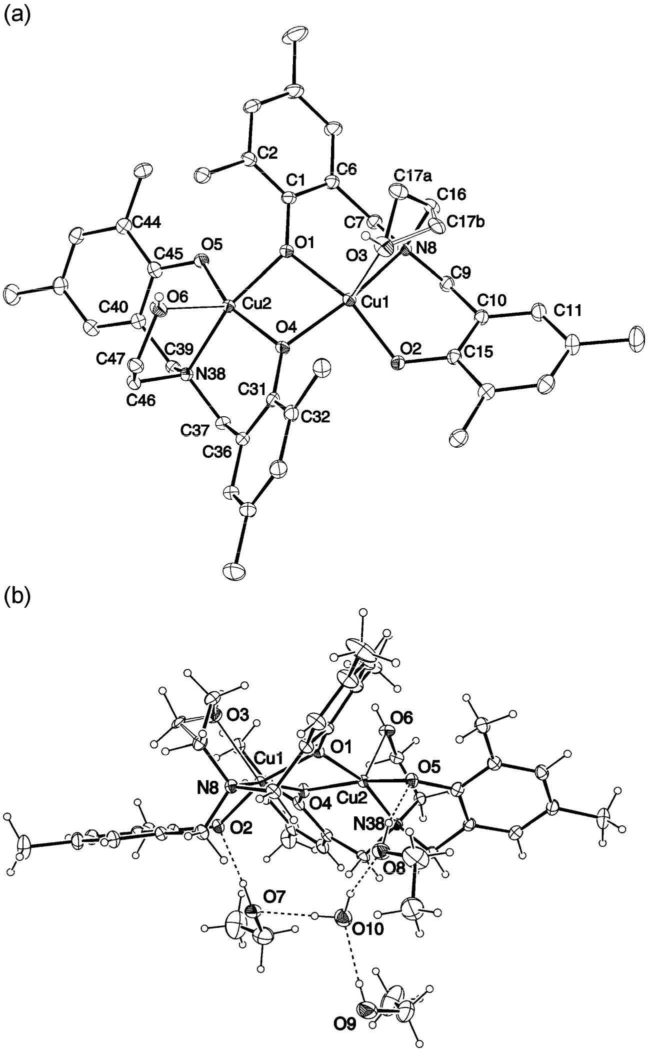


Figure 1. (a) Molecular structure of [$Cu_2(HL1)_2$]·3EtOH·H_2O (**1**); thermal ellipsoids are drawn at the 30% probability level; ethanol and water molecules are not shown; CH hydrogen atoms are omitted for clarity; (b) side view of **1** showing the hydrogen-bonding interactions.

Crystal Structure of [$Cu_2(HL2)_2$]·1.65H_2O (2)

This compound crystallizes in an orthorhombic space group with a symmetric binuclear Cu_2-(μ-OPh)$_2$ rectangular core (Figure 2a). Important bonding parameters are presented in Table 2. The ligands coordinate in a tridentate/bridging manner to the copper centres, forming a distorted square-planar coordination sphere with two μ_2-phenoxido oxygen atoms, an amine nitrogen atom and a phenoxido oxygen atom. The unit cell contains also two noncoordina-

Table 1. Selected bond lengths [Å] and angles [°] for **1**.

Cu1		Cu2	
Cu1–O1	1.946(2)	Cu2–O1	1.972(2)
Cu1–O4	1.983(2)	Cu2–O4	1.955(2)
Cu1–O2	1.904(2)	Cu2–O5	1.900(2)
Cu1–O3	2.322(3)	Cu2–O6	2.321(2)
Cu1–N8	2.057(2)	Cu2–N38	2.051(3)
O1–Cu1–O2	162.76(9)	O4–Cu2–O5	159.77(9)
O1–Cu1–O4	75.64(8)	O1–Cu2–O4	75.71(8)
O1–Cu1–N8	93.39(9)	O4–Cu2–N38	94.45(9)
O2–Cu1–N8	95.37(10)	O5–Cu2–N38	95.59(10)
O2–Cu1–O4	91.51(9)	O1–Cu2–O5	90.80(9)
O1–Cu1–O3	95.96(10)	O1–Cu2–O6	111.74(9)
O2–Cu1–O3	100.25(10)	O5–Cu2–O6	105.65(9)
O3–Cu1–O4	117.71(9)	O4–Cu2–O6	93.46(9)
O3–Cu1–N8	79.18(9)	O6–Cu2–N38	79.14(9)
O4–Cu1–N8	160.25(10)	O1–Cu2–N38	165.41(9)
Cu1···Cu2	3.0231(5)		
Cu1–O1–Cu2	101.00(9)	Cu1–O4–Cu2	100.31(9)

Table 2. Selected bond lengths [Å] and angles [°] for **2**–**5**.

Compound[a]	**2**	**3**	**4**	**5**
Cu–O1	1.9217(16)	1.934(2)	1.928(2)	1.9312(15)
Cu–O1^{i}	1.9906(15)	1.963(2)	1.963(2)	2.0017(16)
Cu–O2	1.8754(15)	1.894(2)	1.876(2)	1.8996(16)
Cu–N8	2.031(2)	2.011(2)	2.005(2)	2.026(2)
Cu–O4		2.525(3)		2.5797(3)
O1–Cu–O2	166.17(7)	166.16(9)	160.31(9)	169.52(7)
O1–Cu–O1^{i}	74.95(7)	76.57(10)	76.57(10)	76.01(8)
O1–Cu–N8	95.53(7)	94.38(9)	94.83(10)	93.33(7)
O1^{i}–Cu–N8	162.27(7)	165.73(10)	169.92(9)	169.14(7)
O2–Cu–N8	97.73(7)	96.75(9)	97.33(10)	97.11(7)
O2–Cu–O1^{i}	91.22(7)	93.96(9)	92.39(9)	93.58(7)
Cu···Cu^{i}	2.9620(5)	2.8704(7)	2.9568(7)	2.8475(5)
Cu–O1–Cu^{i}	98.40(7)	94.89(9)	98.92(9)	92.76(7)
Cu–O4–Cu^{i}		69.29(9)		67.00(7)

[a] Symmetry code *i* for **2**, **3**, **4** and **5** is $x, -y, 1-z$; $-x, y, 3/2-z$; $1-x, y, 3/2-z$; $2-x, y, 3/2-z$, respectively.

ting water molecules, one of which is partly populated (65%). The side view of the molecule is presented in Figure 2b.

Crystal Structure of [$Cu_2(HL3)_2(H_2O)$] (3)

This complex crystallizes in the monoclinic space group with a symmetric binuclear Cu_2-(μ-OPh)$_2$ rectangular core (Figure 3a). Relevant bonding parameters are presented in Table 2. The ligands coordinate in a tridentate/bridging

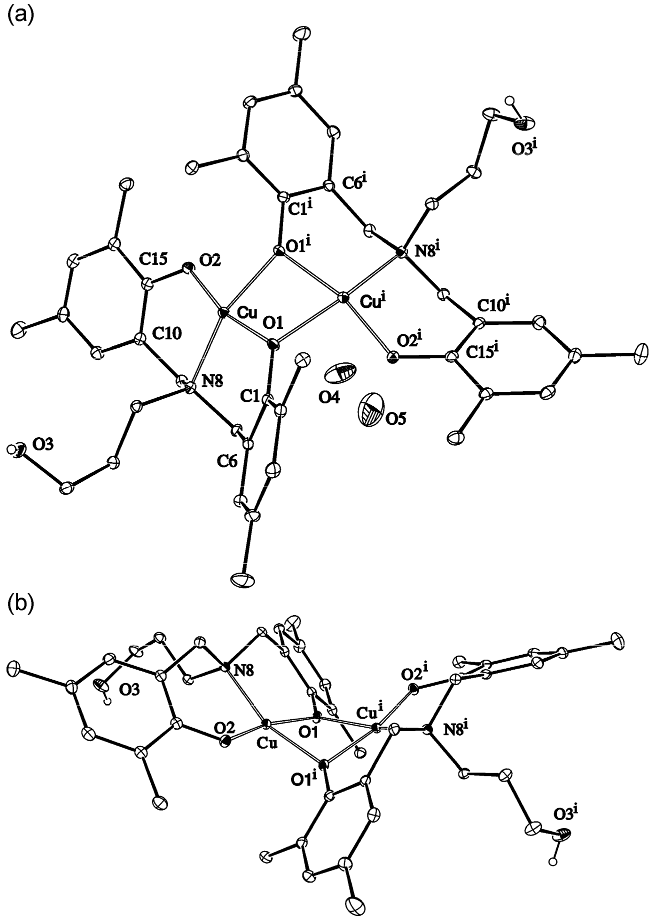


Figure 2. (a) Molecular structure of [$Cu_2(HL2)_2$]·1.65H_2O (**2**); thermal ellipsoids are drawn at the 30% probability level; CH hydrogen atoms and hydrogen atoms at the water molecules are omitted for clarity; symmetry operation i:= $x, -y, 1-z$; (b) side view of **2** without water molecules.

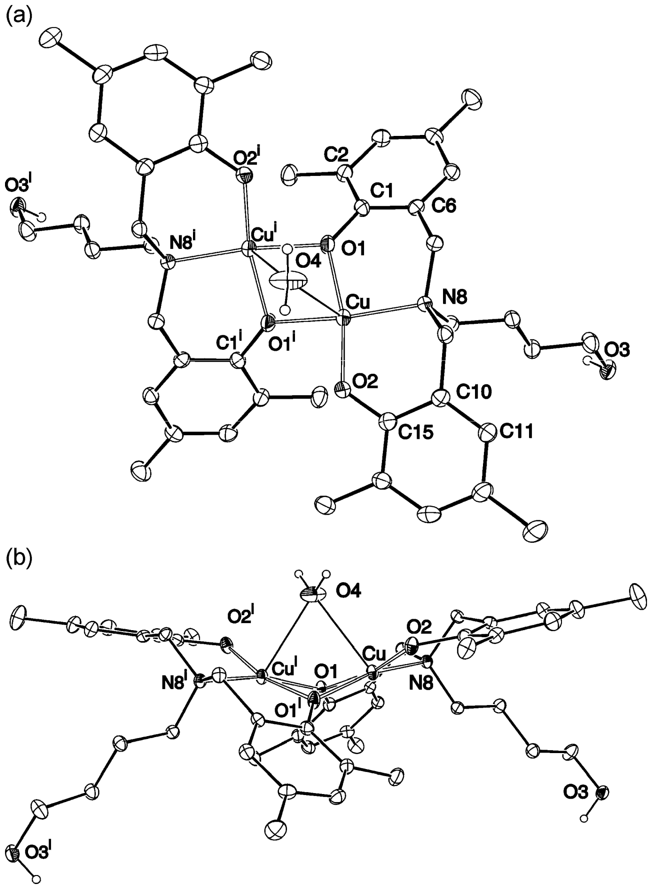


Figure 3. (a) Molecular structure of [$Cu_2(HL3)_2(H_2O)$] (**3**); thermal ellipsoids are drawn at the 30% probability level; CH hydrogen atoms are omitted for clarity; symmetry operation i: $-x, y, 1.5-z$; (b) side view of **3** showing the position of the coordinated water molecule, which forms a bridge between copper(II) ions.

manner to the copper centres as in **2** with two μ_2-phenoxido oxygen atoms, an amine nitrogen atom and a phenoxido oxygen atom. The weakly coordinated water molecule forms a bridge between the copper(II) ions. Thus, coordination around the copper(II) ion can be also considered as a distorted (4+1) five-coordination (square-base pyramid). The side view of the molecule is presented in Figure 3b. The bridging water molecules, the oxygen atoms of the amino alcohol groups and the nonbridging phenolate groups are involved in hydrogen-bonding interactions.

Crystal Structure of [$Cu_2(HL4)_2$] (4)

This complex crystallizes in the monoclinic space group with a symmetric binuclear Cu_2-(μ-OPh)$_2$ rectangular core (Figure 4a). Important bonding parameters are presented in Table 2. The ligands coordinate in a tridentate/bridging manner to the copper centres as in **2**. The side view of the molecule is presented in Figure 4b. The geometry and the roof shape of the coordination plane in **4** resemble those in the copper(II) complex of 2-{bis[(3,5-di-*tert*-butyl-2-hydroxybenzyl)amino]methyl}tetrahydrofuran.[6k]

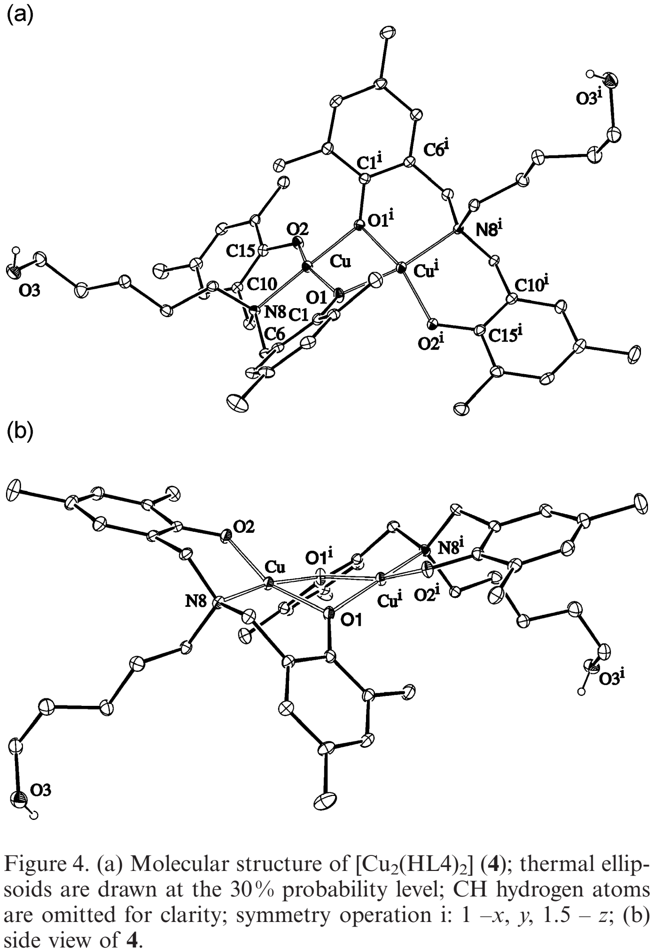


Figure 4. (a) Molecular structure of [$Cu_2(HL4)_2$] (**4**); thermal ellipsoids are drawn at the 30% probability level; CH hydrogen atoms are omitted for clarity; symmetry operation i: 1 –*x*, *y*, 1.5 – *z*; (b) side view of **4**.

Crystal Structure of [$Cu_2(HL5)_2(H_2O)$] (5)

This compound crystallizes in the monoclinic space group with a structure quite similar to that of compound **3** (Figure 5a). Relevant bonding parameters are presented in Table 2. The side view of the molecule is presented in Figure 5b.

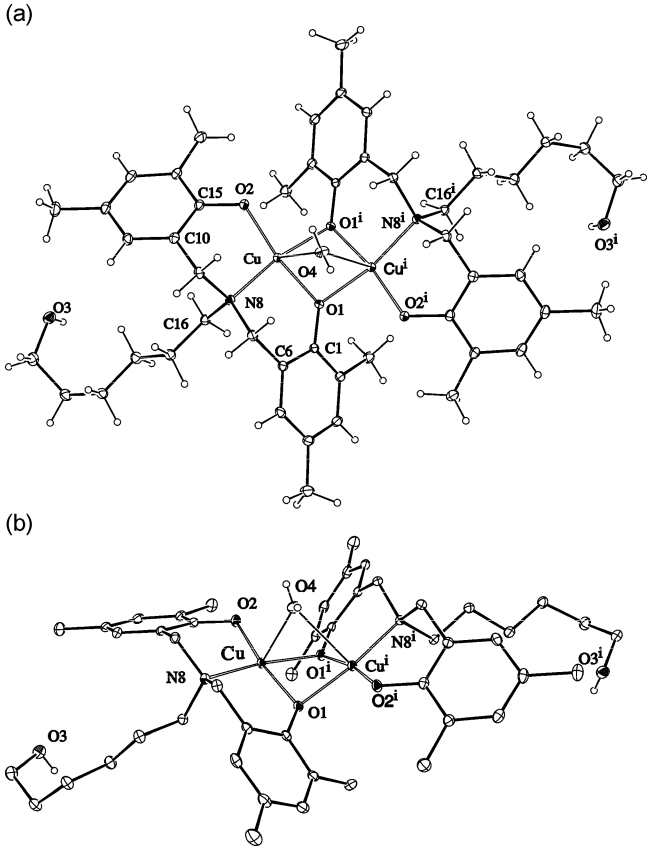


Figure 5. (a) Molecular structure of [$Cu_2(HL5)_2(H_2O)$] (**5**); thermal ellipsoids are drawn at the 30% probability level; CH hydrogen atoms are omitted for clarity; symmetry operation i: 2 – *x*, *y*, 1.5 – *z*; (b) side view of **5**.

Magnetic Properties of the Complexes

Complexes **1**, **2** and **4** were found to be weakly paramagnetic even at room temperature, indicating very strong antiferromagnetic interactions occurring between the copper(II) ions through the phenoxido bridges. In fact, no maximum was observed in their respective χ_M vs. T plots and, therefore, J must be greater than $\approx$–400 cm^{-1}. However, the χ_M vs. T plots (χ_M is the molar susceptibility for the Cu_2 unit) for **3** and **5** (Figures 6 and 7) show a maximum at 270 and 87 K, respectively, indicating the existence of strong and moderate antiferromagnetic interactions between the copper(II) ions, respectively. Below the temperature of the maximum, χ_M decreases with a decrease in the temperature. At very low temperatures, however, χ_M increases, which is typical of these strong AF coupled systems, and indicates the presence of a small amount of paramagnetic impurity. As expected, the $\chi_M T$ product at room temperature for both compounds is much lower than that expected for two uncoupled copper(II) ions with $g = 2$ (0.750 cm^3 mol^{-1} K). Upon lowering the temperature, the $\chi_M T$ product rapidly decreases close to zero at 2 K. The susceptibility data for **1**–**5** were fitted to the Bleaney–Bowers equation with the Hamiltonian $H = -JS_1S_2$. A ρ parameter was included in the theoretical equation to account for the percentage of paramagnetic impurity. The best-fit parameters are given in Table 3. It should be noted that for compounds **1**, **2** and **4**, the uncertainty in the estimation of the J value from the fit of the susceptibility data is very large, as the diamagnetic correction is of the same order of magnitude as the uncorrected molar susceptibility. In view of this, the estimated J values for **1**, **2** and **4** must be taken with caution. With regard to **3** and **5**, which contain triply bridged copper(II) atoms (two phenoxido bridges and a water bridge), the interaction through the water bridge is considered to be negligible, as the Cu–O$_w$ distance are too long and the O$_w$ is coordinated at axial position where the spin density of the unpaired electron (located at the $d_{x^2-y^2}$ magnetic orbital, which is directed towards the donor atoms in the equatorial/basal plane) is, if any, very poor (see the spin density diagram in Figure 8).

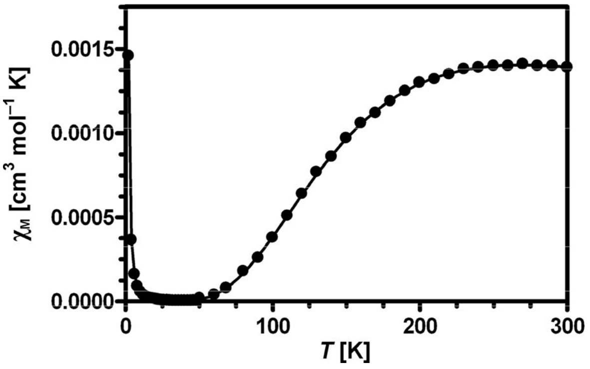


Figure 6. Temperature dependence of χ_M for complex **3**.

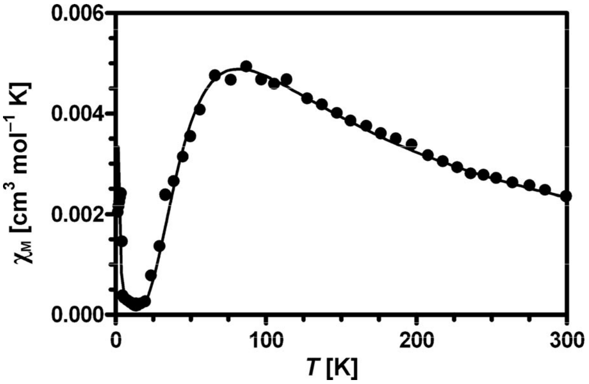


Figure 7. Temperature dependence of χ_M for complex **5**.

Both theoretical and experimental studies have shown that the major factor controlling the magnetic exchange interaction in dialkoxido-bridged dicopper(II) complexes is the value of the Cu–O–Cu angle, and an almost linear variation of J with θ (the Cu–O–Cu angle) has been established. DFT calculations carried out on alkoxido-bridged model compounds,[3–5] containing a planar Cu$_2$(μ-O$_2$) skeleton and a methyl group bonded to each oxygen atom of the double bridge, predicted antiferromagnetic interactions for the whole range of Cu–O–Cu (θ) when τ values (out-of-plane displacement of the phenyl carbon atom from the Cu$_2$O$_2$ plane) were smaller than 40°.[4c] Moreover, a correlation was established between θ and τ, showing that small

Table 3. Structural and magnetic data for complexes **1**–**5**.

Complex	Cu···Cu [Å]	Cu–O–Cu θ [°]	δ[a]	τ[b] [°]	γ[c] [°]	ω[d] [°]	$J_{exp.}$ [cm^{-1}] g ρ	$J_{calcd.}$ [cm^{-1}]
1	3.0231(5)	100.66(9)	(4+1) 0.04 0.09	1.0(2) 11.7(3)	25.9(1)	44.36(6)	–470.8 2.082 0.006	–443.2
2	2.9620(5)	98.41(7)	4 0.77	2.3(2) 354.2[e]	34.94(5)	47.12(4)	–417.5 2.105 0.003	–387.7
3	2.8704(7)	94.89(9)	(4+1) 0.007	23.9(2) 360.0	40.41(7	43.03(6)	–300.1 2.015 0.01	–271.4
4	2.9571(7)	98.93(10)	4 0.79	28.6(2) 358.3	29.00(6)	40.00(5)	–462.3 2.19 0.006	–396.4
5	2.8475(5)	92.76(7)	(4+1) 0.007	2.5(2) 347.7	46.54(6)	47.17(4)	–91.2 2.080 0.02	–107.3

[a] The distortion of the coordination geometry for five-coordinated complexes [marked with (4+1)] is $\delta = (\alpha - \beta)/60$ (α and β are the larger trans X–Cu–X angle, δ is 1 for a trigonal-bipyramidal geometry and 0 for square-pyramid).[18] For four-coordinated complexes (marked with 4) ($\delta = \Delta/70.5$, Δ being the difference between the mean value of the *trans* X–Cu–X angles and the ideal tetrahedral angle of 109.5°; δ = 0 for the ideal tetrahedral geometry and δ = 1 for the ideal square-planar geometry). [b] τ is the substituents angle from the bridging O···O-line. [c] γ the dihedral angle of the bridge O–Cu–O planes (only atoms Cu, O and O′). [d] ω the dihedral angle between the coordination planes of Cu^{II} ions. [e] Sum of the angles around O$_{phenoxido}$.

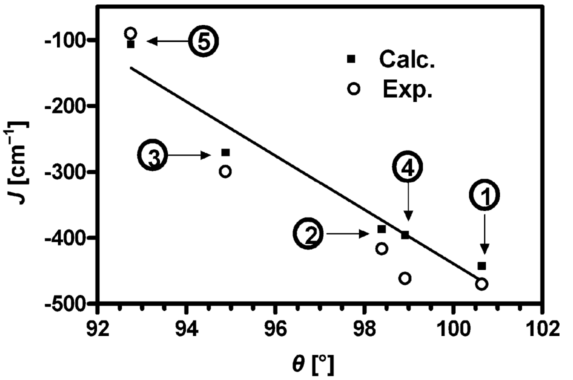


Figure 8. Calculated and experimental magnetic exchange coupling for **1**–**5**. The solid line represents the linear relationship between the calculated J and θ values.

values of θ are associated with the largest values of τ. Therefore, the AF coupling is favoured when θ increases and τ decreases. In the case of the bis(μ-phenoxido)dicopper(II) complexes, experimental results[6] revealed the dependence of J on several structural factors: (i) the Cu–O(phenolato)–Cu angle (θ); (ii) the τ value (out-of-plane displacement of the phenyl carbon atom from the Cu_2O_2 plane); (iii) the dihedral angle of the bridge O–Cu–O planes; (iv) the deviation of the copper(II) coordination geometry from square-pyramid or square-planar; (v) the dihedral angle between the coordination planes of the Cu^{II} atoms; (vi) the Cu···Cu distance. As in bis(μ-alkoxido)dicopper(II) complexes, the AF magnetic exchange increases when θ increases and τ decreases. Likewise, the AF coupling increases when the distortion from square-pyramid or square-planar and the dihedral angle between the coordination planes of the copper(II) ions decrease. Amongst the above factors, the θ angle is considered to be the main structural parameter responsible for the magnetic coupling in bis(μ-phenoxido)dicopper(II) complexes. It should be noted, as indicated elsewhere, that the major part of (μ-phenoxido)dicopper(II) complexes exhibited antiferromagnetic spin coupling (only in five instances a weak ferromagnetic coupling was observed).

Complexes **1**–**5** are made from a family of ω-[bis(2-hydroxy-3,5-dimethylbenzyl)amino]alkan-1-ol ligands bearing an increasing number of carbon atoms in the backbone of the aminoalkyl moiety (from $n = 2$ in complex **1** to $n = 6$ in complex **5**). All the complexes have a similar planar Cu(μ-$O_{phenoxido}$)$_2$Cu bridging skeleton and coordination geometries around copper(II) ions that are close to either square-planar (compounds **2** and **4**) or square-pyramid (see Table 5). The trend of the J values observed for **1**–**5** can be explained by the key structural parameters (i)–(v) (see above). Thus, complex **1**, with larger θ and lower τ values is expected to exhibit a stronger AF interaction (–470.8 cm^{-1}). Moreover, the low γ value (Table 3) also favours a much stronger AF interaction in **1**. Complexes **2** and **4** possess very similar θ values of about 98°. Although the τ angle is very small for **2**, the smaller θ and higher γ and ω values favour a lower AF interaction in this compound than in **4**. Complexes **3** and **5** exhibit lower θ values and, in consequence, smaller values of J. Complex **5**, in addition to having the smallest θ angle found for complexes **1**–**5**, has the highest values of γ and ω angles, and therefore, it exhibits the weaker AF interaction (–91.2 cm^{-1}).

We also decided to perform DFT/B3LYP[7] theoretical calculations to evaluate the magnetic exchange coupling constants and to check the experimental values. For that, we employed Jaguar 7.5[8] and Gaussian 03 (revision E.01)[9] software, using the Ahlrichs all-electron TZV basis set[10] for all the atoms. The J values were obtained as the intrinsic energy difference between the broken symmetry singlet state and the corresponding triplet state by means of single-point calculations from the crystallographic geometries. The computed J values for **1**–**5** are given in Table 4 and compare reasonably well with the experimental values. The calculated values of J (Table 3) for **1**–**5** are presented in Figure 7 as a function of the θ angle. As it can be observed, there is an almost linear relationship between J and θ despite the significant differences in the τ, γ and ω angles and the Cu···Cu distances for **1**–**5**. This is a good supporting evidence that in bis(μ-phenoxido)dicopper(II) systems where the phenoxido bridge connects two equatorial positions on the copper(II) atoms, the main structural factor controlling the magnetic exchange interactions is, by far, the value of the θ angle.

Table 4. Mulliken spin densities for copper atoms and bridging phenoxido oxygen atoms in complexes **1**–**5**.

Spin densities	1	2	3	4	5
Cu1	0.6139	0.5695	0.6048	0.5781	0.5824
Cu2	–0.6117	–0.5695	–0.6049	–0.5781	–0.5825
O1	–0.0005	0.0059	0.0184	0.0140	0.0068
O2	–0.0094	–0.0059	–0.0184	–0.0140	–0.0068

For complexes **1**–**5** containing ω-[bis(2-hydroxy-3,5-dimethylbenzyl)amino]alkan-1-ol ligands, the crossover point below which the magnetic behaviour changes from AF to F coupling is predicted at ca. 89°. In good agreement with this prediction, a member of this family of dinuclear copper(II) complexes, containing the ligand [bis(3,5-di-*tert*-butyl-2-hydroxybenzyl)amine, presents Cu–$O_{phenoxido}$–Cu angles of ≈86° and a ferromagnetic interaction of +26.3 cm^{-1}. In this case, the high value of the γ angle (75.4°) also favours the ferromagnetic interaction.[6j] In another bis(μ-phenoxido)dicopper(II) complex, containing the closely related 2-{bis[(3,5-di-*tert*-butyl-2-hydroxybenzyl)-amino]methyl}tetrahydrofuran ligand,[6k] the θ angles are slightly higher (≈88°) and the J value is –12.0 cm^{-1}. These results support the validity of our calculations.

The calculated spin density for the ground singlet state of **1**–**5** offers information on the electronic structure and the mechanism of the magnetic exchange interaction. The spin densities for **1**–**5** (Table 4), obtained from the broken symmetry (BS) singlet state (the spin density of **1** is given as an example in Figure 9, whereas those for **2**–**5** are given in the Supporting Information), clearly show that the spin density at each copper(II) atom has the shape of a $d_{x^2-y^2}$ orbital (as expected for quasi square-pyramid and square-planar geometries), and it is σ delocalized on the donor atoms directly attached to the metal. Therefore, exchange pathway is of the σ type, involving the $d_{x^2-y^2}$ magnetic orbitals of the copper(II) atoms and the p orbitals of the bridging oxygen atoms.

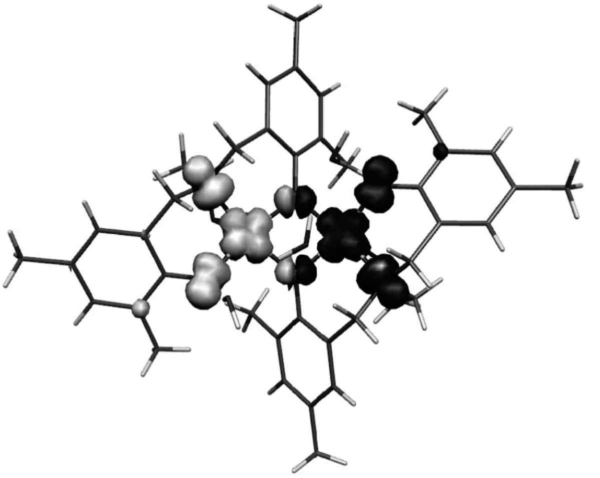


Figure 9. Calculated spin density distribution for the singlet broken-symmetry state of **1**. Light grey shapes correspond to positive and black shapes to negative spin densities. The isodensity surface corresponds to a cut-off value of 0.002 e bohr^{-3}.

As it can be observed in Table 4, in the BS singlet the spin densities on the two Cu^{II} centres have opposite signs and close absolute values: Cu1 atoms are mainly populated by the unpaired electron with α spin, whereas the Cu2 atoms are mainly populated by the unpaired electron with β spin. The atoms of the terminal ligands bonded to the Cu^{II} centres have spin densities with the same sign as the copper(II) atoms to which they are bonded, which indicates that a spin delocalization has taken place for the unpaired electrons on the Cu^{II} ions. In the case of the phenoxido oxygen atoms, with the exception of compound **1** where O2 is mainly affected by the β spin delocalization, O1 has α spin and O2 β spin, showing a symmetrical distribution. Anyway, the spin density delocalized on the oxygen atoms of the bridging region is small and, therefore, the spin density is mainly found at the metal ions. This fact indicates that the two copper(II) atoms are indeed the magnetic centres.

Conclusions

We demonstrated that copper(II) ion reacts with a family of ω-{[bis(2-hydroxy-3,5-dimethylphenyl)methyl]amino}-alkan-1-ol ligands to afford five new bis(μ-phenoxido)dicopper(II) complexes with a Cu_2-(μ-OPh)$_2$ rectangular core, and in which the oxygen bridging atoms connect equatorial positions on the distorted square planar or square-pyramidal copper(II) coordination spheres. The copper coordination environments and geometries are modified when the number of carbon atoms in the backbone of the aminoalkanol chain increases on going from **1** to **5**. The coordination planes (Cu atom and four strongly bonded donors) around the Cu atoms in the dinuclear units form a roof-like structure with variable roof angle [folding the coordination planes though O atoms in the Cu_2(μ-OPh)$_2$ bridge]. By contrast, hydroxide and alkoxide groups generally bridge metal ions in their complexes with planar Cu_2O_2 entities. Magnetic studies of these dinuclear complexes showed that J values vary from –470.8 to –91.2 as the Cu–O–Cu angles (θ) vary from 100.66(9) to 92.76(7)°. The trend of the J values observed for **1**–**5** can be explained by the key structural parameters of the Cu_2(μ-OPh)$_2$ bridging unit. DFT theoretical calculations produced the corresponding magnetic exchange coupling constants, which are quite near to the experimental ones. Despite the significant differences in the τ, γ and ω angles and Cu···Cu distances for **1**–**5** an almost linear relationship between the calculated J values with θ could be established. This is good supporting evidence that in bis(μ-phenoxido)dicopper(II) systems where the phenoxido bridge connects two equatorial positions on the copper(II) atoms, the main structural factor controlling the magnetic exchange interactions being by far the value of the θ angle. The crossover point below which the magnetic behaviour changes from AF to F coupling is predicted at ca. 89°. Experimental results for bis(μ-phenoxido)dicopper(II) complexes with closely related ligands support the validity of this prediction.

Experimental Section

General Information: Starting materials for all syntheses were purchased from Aldrich, Merck or Riedel and were of reagent grade and used as received. Solvents were of HPLC grade and used as purchased. All syntheses were performed under ambient laboratory atmosphere. The NMR spectra were recorded with a Bruker Avance DPX 250 FTNMR spectrometer or with a Bruker Avance DRX 500 FTNMR spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded either in $CDCl_3$, [D$_6$]DMSO or CD_3OD at 30 °C. The chemical shifts are reported in ppm and referenced internally by using the residual protic solvent resonances relative to tetramethylsilane ($CDCl_3$: δ = 7.26 ppm, ^{1}H NMR; δ = 77.0 ppm, ^{13}C NMR; [D$_6$]DMSO: δ = 2.50 ppm,^{1}H NMR; δ = 39.50 ppm, ^{13}C NMR; CD_3OD: δ = 3.30 ppm, ^{1}H NMR; δ = 49.0 ppm, ^{13}C NMR). IR spectra were recorded with a Mattson Satellite FTIR spectrometer in KBr discs. Elemental analysis was performed by using a Vario El III elemental analyzer. Single-crystal X-ray measurements were performed by using an Enraf Nonius Kappa CCD area detector diffractometer with the use of graphite monochromated Mo-K_α radiation. Variable-temperature (1.9–300 K) magnetic susceptibility measurements on polycrystalline samples were carried out with a Quantum Design Squid MPMSXL-5 device operating at 1 T from room temperature to 50 K and at 0.05 T from this latter temperature to 2 K. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms by using Pascal's tables.

Ligand and Complex Syntheses: The ligands H_3L1, H_3L2[11] and H_3L3·HCl, H_3L4·HCl[12] were prepared according to known procedures. The ligand H_3L5·HCl is new and was prepared by using a method described below.

***N*,*N*-Bis(2-hydroxy-3,5-dimethylbenzyl)-6-aminohexanol·HCl:** A 25-mL decanter flask was charged with 2,4-dimethylphenol (2.69 g, 0.022 mol), paraformaldehyde (0.66 g, 0.022 mol) and 6-amino-1-hexanol (1.18 g, 0.010 mol). The decanter was put into an oven (T = 120°) and was kept for 145 min. The formed yellow syrup was dissolved in methanol (10 mL), moved to a 50-mL round-bottomed flask and treated with HCl (4 mL, 6 M). The solvent was evaporated under reduced pressure, and diethyl ether (10 mL) and water (10 mL) were successively added to the resulting syrup. The aqueous phase was separated and extracted with diethyl ether (2 × 10 mL), which resulted in the precipitation of the product. White flakes were filtered off, washed with water (10 mL) and recrystallized from acetonitrile/methanol (10:3). Yield: 2.05 g (49%). ^{1}H NMR (500 MHz, CD_3OD): δ = 1.29 (m, 4 H, $NCH_2CH_2CH_2CH_2$), 1.47 (m, 2 H, NCH_2CH_2), 1.81 (m, 2 H, CH_2CH_2OH), 2.21 and 2.23 (s, 12 H, aryl-CH_3), 3.15 (t, 2 H, NCH_2CH_2), 3.50 (t, 2 H, CH_2OH), 4.33 (d, 4 H, $ArCH_2NCH_2Ar$), 6.92 (s, 2 H, Ar*H5*), 7.01 (s, 2 H, Ar*H3*) ppm. ^{13}C NMR (500 MHz, CD3OD): δ = 16.49 and 20.51 (aryl CH_3), 25.29, 26.25, 27.07, 33.27 ($NCH_2CH_2CH_2CH_2CH_2$), 54.77 (NCH_2CH_2), 57.21 ($ArCH_2NCH_2Ar$), 62.72 (CH_2OH), 118.89, 126.44, 131.01, 131.48, 134.83, 152.91 (Aryl C) ppm. $C_{24}H_{36}ClNO_3$ (422.01): calcd. C 68.31, H 8.60, N 3.32; found C 68.64, H 8.54, N 3.28.

[$Cu_2(HL1)_2$]·3EtOH·H_2O (1): Complex **1** was prepared by dissolving H_3L1 (0.040 g, 0.12 mmol), Et_3N (34 µL, 0.24 mmol) and $Cu(NO_3)_2$·$3H_2O$ (0.024 g, 0.10 mmol) in 70% EtOH (7 mL). The resulting brownish dark green solution was kept at room temperature for one week, leading to the formation of dark green crystals. The crystals were filtered off and air dried. The crystals are soluble in $CHCl_3$, diethyl ether and acetone. Yield: 0.032 g (66%). IR (KBr): $\tilde{\nu}$ = 3208 (w), 2989 (m), 2908 (m), 2854 (m), 1610 (w), 1475 (s), 1311 (m), 1251 (s), 1160 (m), 1089 (w), 858 (m), 804 (m), 609 (w), 499 (w) cm^{-1}. Data for [$Cu_2(HL1)_2$]: $C_{40}H_{50}Cu_2N_2O_6$ (781.94): calcd. C 61.44, H 6.45, N 3.58; found C 60.94, H 6.43, N 3.19. A single-crystal X-ray analysis was performed on one of these crystals.

[$Cu_2(HL2)_2$]·1.65H_2O (2): Complex **2** was prepared by dissolving H_3L2 (0.039 g, 0.11 mmol), Et_3N (31 µL, 0.22 mmol) and $Cu(NO_3)_2$·$3H_2O$ (0.024 g, 0.10 mmol) in 70% EtOH (6 mL). The resulting brownish green solution was kept at room temperature for one week leading to the formation of dark green crystals. The crystals were filtered off and air dried. The crystals are soluble in $CHCl_3$. Yield: 0.032 g (77%). IR (KBr): $\tilde{\nu}$ = 3307 (w), 3226 (w), 2987 (w), 2940 (m), 2912 (m), 2856 (m), 1745 (w), 1608 (w), 1544 (w), 1471 (s), 1440 (m), 1382 (w), 1309 (m), 1243 (m), 1153 (m), 1093 (m), 862 (m), 804 (m), 615 (w), 505 (w) cm^{-1}. Data for [$Cu_2(HL2)_2$]·1.65H_2O: $C_{42}H_{56}Cu_2N_2O_7$ (828.00): calcd. C 60.92, H 6.82, N 3.38; found C 60.73, H 6.89, N 3.10. A single-crystal X-ray analysis was performed on one of these crystals.

[$Cu_2(HL3)_2(H_2O)$] (3): Complex **3** was prepared by dissolving 0.044 g (0.11 mmol) of H_3L3·HCl, 46 µL (0.33 mol) of Et_3N and 0.024 g (0.10 mmol) of $Cu(NO_3)_2$·$3H_2O$ in 6 mL of 70% EtOH (v/v). The resulting dark green solution was kept at room temperature for one week leading to the formation of dark green crystals. The crystals were filtered off and air dried. Yield 0.036 g (84%). The crystals are slightly soluble in $CHCl_3$, EtOH and MeOH. IR (KBr): $\tilde{\nu}$ = 3392 (m), 2994 (m), 2910 (s), 2863 (s), 1612 (w), 1475 (s), 1382 (m), 1309 (s), 1253 (s), 1162 (m), 1062 (m), 860 (m), 806 (s), 615 (m), 499 (m) cm^{-1}. Data for [$Cu_2(HL3)_2(H_2O)$]: $C_{44}H_{60}Cu_2N_2O_7$ (856.06): calcd. C 61.73, H 7.06, N 3.27; found C 61.77, H 7.17, N 3.00. A single-crystal X-ray analysis was performed on one of these crystals.

[$Cu_2(HL4)_2$] (4): Complex **4** was prepared by dissolving H_3L4·HCl (0.049 g, 0.12 mmol), Et_3N (50 µL, 0.36 mmol) and $Cu(NO_3)_2$·$3H_2O$ (0.024 g, 0.10 mmol) in 99.5% EtOH (3 mL). To the resulting dark green solution was added water (2.5 mL), leading to the formation of a green solid, which disappeared after vigorous stirring. This solution was kept at room temperature for one week, leading to the formation of the dark green crystals. The crystals were filtered off and air dried. The crystals are soluble in $CHCl_3$, EtOH and MeOH. Yield: 0.038 g (88%). IR (KBr): $\tilde{\nu}$ = 3322 (w), 2992 (w), 2913 (m), 2858 (m), 1612 (w), 1479 (s), 1382 (w), 1311 (m),

Table 5. Summary of crystallographic data for **1**–**5** at 173(2) K.

Complex	**1**	**2**	**3**	**4**	**5**
Formula	$C_{46}H_{70}Cu_2N_2O_{10}$	$C_{42}H_{57.3}Cu_2N_2O_{7.65}$	$C_{44}H_{60}Cu_2N_2O_7$	$C_{46}H_{62}Cu_2N_2O_6$	$C_{48}H_{68}Cu_2N_2O_7$
M_r	938.14	839.70	856.02	866.06	912.12
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
Space group (no.)	$P2_1/a$ (14)	*F2dd* (43)	*C*2/*c* (15)	*C*2/*c* (15)	*C*2/*c* (15)
a [Å]	17.4756(3)	14.5559(3)	17.5592(7)	18.3534(6)	19.8787(3)
b [Å]	15.4651(3)	18.9918(4)	13.7279(5)	14.2742(5)	9.6564(3)
c [Å]	18.0543(3)	29.0799(6)	18.8162(7)	17.9932(6)	23.6054(6)
α [°]	90	90	90	90	90
β [°]	96.764(1)	90	109.906(2)	114.230(2)	99.913(2)
γ [°]	90	90	90	90	90
V [Å^3]	4845.4(2)	8038.9(3)	4264.7(3)	4298.6(3)	4463.6(2)
Z	4	8	4	4	4
$D_{calcd.}$ [g cm^{-3}]	1.286	1.398	1.333	1.338	1.357
μ(Mo-K_α) [cm^{-1}]	9.33	11.12	10.48	10.39	10.06
Observed reflections	9490	3871	5111	4179	5388
R_{int}	0.0757	0.0471	0.0778	0.0788	0.0558
Parameters	576	260	260	256	277
R_1[a]	0.0790 (0.0465)[b]	0.0273 (0.0253)	0.1059 (0.0550)	0.0705(0.0443)	0.0676 (0.0458)
wR_2[c]	0.1131 (0.1004)	0.0607 (0.0599)	0.1125 (0.0984)	0.1017 (0.0929)	0.1059 (0.0982)
Largest difference in peak and hole [e Å^{-3}]	0.560 to –0.392	0.415 to –0.230	0.382 to –0.319	0.333 to –0.322	0.389 to –0.504

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] Values in parentheses for reflections with $I > 2\sigma(I)$. [c] $wR_2 = \{\Sigma[w(F^2_o - F^2_c)^2]/\Sigma[w(F^2_o)^2]\}^{1/2}$ and $w = 1/[\sigma^2(F^2_o) + (aP)^2 + (bP)]$, where $P = (2F^2_c + F^2_o)/3$.

1251 (m), 1160 (m), 1072 (w), 962 (w), 858 (w), 804 (m), 613 (w), 501 (w) cm^{-1}. Data for [$Cu_2(HL4)_2$]: $C_{46}H_{62}Cu_2N_2O_6$ (866.10): calcd. C 63.79, H 7.22, N 3.23; found C 64.35, H 7.38, N 3.00. A single-crystal X-ray analysis was performed on one of these crystals.

[$Cu_2(HL5)_2(H_2O)$] (5): Complex **5** was prepared by dissolving $H_3L5{\cdot}HCl$ (0.051 g, 0.120 mmol), Et_3N (50 µL, 0.36 mmol) and $Cu(NO_3)_2{\cdot}3H_2O$ (0.024 g, 0.10 mmol) in 99.5% EtOH (3 mL). To the resulting dark green solution was added water (0.5 mL), and this solution was kept at room temperature for three weeks, leading to the formation of dark green crystals. The crystals were filtered off and air dried. The crystals are soluble in $CHCl_3$, EtOH and MeOH. Yield: 0.030 g (65%). IR (KBr): $\tilde{\nu}$ = 3334 (m), 3205 (m), 2992 (m), 2921 (s), 2859 (s), 1612 (w), 1474 (s), 1309 (s), 1249 (s), 1160 (m), 1051 (m), 852 (m), 804 (s), 609 (m), 553 (m), 509 (m) cm^{-1}. Data for [$Cu_2(HL5)_2(H_2O)$]: $C_{48}H_{68}Cu_2N_2O_7$ (912.16): calcd. C 63.20, H 7.51, N 3.07; found C 63.42, H 7.59, N 2.84. A single-crystal X-ray analysis was performed on one of these crystals.

X-ray Crystallography: Crystals suitable for single-crystal X-ray measurements were obtained directly from the reaction vessels. The crystal data for compounds **1**–**5** are summarized in Table 5 along with other experimental details. The crystallographic data were collected at 173 K with an Enraf Nonius Kappa CCD area-detector diffractometer with the use of graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Data collection was performed by using ϕ and ω scans, and the data were processed by using DENZO-SMN v0.93.0.[13] SADABS[14] absorption correction was applied for compounds. The structures were solved by direct methods by using the SHELXS-97[15] program or the SIR-97[16] program and full-matrix least-squares refinements on F^2 were performed using the SHELXL-97[15] program. Figures were drawn with ORTEP-3 for Windows.[17] For all compounds the heavy atoms were refined anisotropically. The CH hydrogen atoms were included at the calculated distances with fixed displacement parameters from their host atoms (1.2 times of the host atom). The rest of the H atoms were refined with the fixed displacement parameters as the CH hydrogen atoms.

CCDC-738970 (for **1**), -738971 (for **2**), -738972 (for **3**), -738973 (for **4**) and -738974 (for **5**) contain 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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