

Supramolecular Hydrogen-Bond Structures and Magnetic Interactions in Basal-Apical, Dinuclear, Azide-Bridged Copper(II) Complexes

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The synthesis, characterisation, X-ray single crystal structures and magnetic properties of three new basal-apical μ_2 -1,1-azide-bridged complexes $[\text{CuL}^1\text{N}_3]_2$ (**1**), $[\text{CuL}^2\text{N}_3]_2$ (**2**) and $[\text{CuL}^3\text{N}_3]_2$ (**3**) with very similar tridentate Schiff-base blocking ligands $\{\text{HL}^1 = N$ -[2-(ethylamino)ethyl]salicylaldehyde; $\text{HL}^2 = 7$ -(ethylamino)-4-methyl-5-azahept-3-en-2-one; $\text{HL}^3 = 7$ -amino-4-methyl-5-azahept-3-en-2-one $\}$ have been reported [complex **1**: monoclinic, $P2_1/c$, $a = 8.390(2)$, $b = 7.512(2)$, $c = 19.822(6)$ Å, $\beta = 91.45(5)^\circ$; complex **2**: monoclinic, $P2_1/c$, $a = 8.070(9)$, $b = 9.787(12)$, $c = 15.743(17)$ Å, $\beta = 98.467(10)^\circ$; complex **3**: monoclinic, $P2_1/n$, $a = 5.884(7)$, $b = 16.147(18)$, $c = 11.901(12)$ Å, $\beta = 90.050(10)^\circ$]. The structures consist of neutral dinuclear entities resulting from the pairing of two mononuclear units through end-on azide bridges connecting an equatorial position of one copper centre to an axial position of the other.

The copper ions adopt a (4+1) square-based geometry in all the complexes. In complex **2**, there is no inter-dimer hydrogen-bonding. However, complexes **1** and **3** form two different supramolecular structures in which the dinuclear entities are linked by H-bonds giving one-dimensional systems. Variable temperature (300–2 K) magnetic-susceptibility measurements and magnetisation measurements at 2 K reveal that all three complexes have antiferromagnetic coupling. Magneto-structural correlations have been made taking into consideration both the azido bridging ligands and the existence of intermolecular hydrogen bonds.

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Introduction

The development of supramolecular structures created by hydrogen bonds is a new challenge for the synthesis of non-serendipitous species in order to study their magnetic behaviour.^[1,2] Control of these hydrogen bonds seems to be very important for synthesising new supramolecular systems. The role played by hydrogen bonds in the transmission of magnetic interactions is still not fully understood. For many years, hydrogen bonds were thought to propagate essentially antiferromagnetic interactions between metal centres,^[3] but the number of ferromagnetically coupled hydrogen-bonded systems is growing.^[1a,4] A variety of ligands have been employed for preparation of these systems. The azido group is one of the most widely used versa-

tile bridges, which is able to create strong hydrogen bonds between itself and OH or NH₂ of the blocking ligands. As a result, azide-bridged complexes, especially those with copper(II), are one of the most fascinating subjects for studying the magnetic interactions.^[5–16] However, there are some misapplications of the magneto-structural correlation for the basal-apical, end-on azide-bridged copper(II) complexes. For example, it is well established that when the azido ligand bridges two Cu^{II} ions in an end-on manner, the nature of the exchange coupling changes from ferromagnetic to antiferromagnetic when the Cu–N–Cu angle is around 108°. ^[17] This correlation, in principle, is valid only for basal-basal coordination, although it has also sometimes been applied to the basal-apical coordination mode. To understand the controlling factors in such systems it is essential to study dinuclear copper(II) compounds. However, among numerous examples of azide-bridged copper(II) complexes, end-on bridged, basal-apical dimers are rare.^[6,10,13] Recently, we found that a group of tridentate Schiff-base blocking ligands, formed by the half condensation of diamines with salicylaldehyde or 2,4-pentandione, provide the desired dimeric species.^[18] We have also shown that for basal-apical coordination, the Cu–N–Cu angle is not indicative of the magnetic interaction, nor does it have any controlling structural parameters; instead the supramolecular

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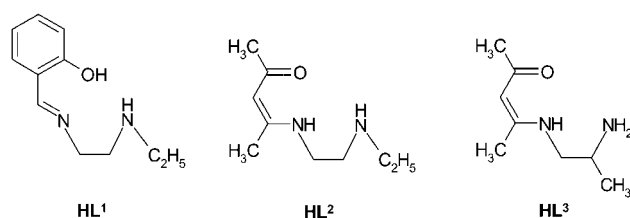
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H-bonding networks between the dinuclear entities play a very important role in magneto-structural correlations.

In order to obtain more insight into the possible control of the H-bonding network and its effect on the magnetism of such systems we have synthesised three new complexes. In this paper we report the synthesis, X-ray crystal-structure analysis, and variable-temperature magnetic behaviour of these basal-apical, dinuclear μ_2 -1,1- N_3 copper(II) complexes with three different tridentate Schiff-base blocking ligands (Scheme 1). We found that very subtle differences in the H-bonding network and structural parameters could be responsible for the drastic changes in magnetic behaviour.



Scheme 1

Results and Discussion

Infrared Spectra

The coordination mode of azide to transition metal is usually detected by the intense IR band due to $\nu_{as}(N_3)$ which occurs above 2000 cm^{-1} . In general, it appears above 2055 cm^{-1} for μ_2 -1,1-azide bridges. However, this generalisation is valid only for symmetric end-on azide bridges where the difference between the two N–N distances ($\Delta d'$) of the azide group is relatively large. In basal-apical-type bridges $\Delta d'$ is smaller and, consequently, ν_{as} appears at lower frequencies.^[13,18] All three complexes (**1**, **2** and **3**) that are reported in this paper show only a single absorption band, consistent with the presence of only one type of azide bridge in the structures, and all of them appear at lower frequencies, viz. 2041 , 2053 and 2043 cm^{-1} respectively, in agreement with the basal-apical bridging.

Complexes **1** and **2** display a single sharp band at 3239 and 3241 cm^{-1} , respectively, due to the N–H stretching vibration whereas complex **3** shows two bands at 3292 and 3247 cm^{-1} characteristic of the NH_2 group. The band cor-

responding to the azomethine ($C=N$) group is distinct in all the three complexes; it occurs at 1630 , 1594 and 1593 cm^{-1} for complexes **1**, **2** and **3**, respectively

Description of Structures of Complexes **1**, **2** and **3**

The structure determination reveals that all the three azido complexes consist of neutral dinuclear entities. Each of them results from the pairing of two mononuclear units related by a crystallographic centre of symmetry. A view of the dinuclear species is given in Figure 1 for complex **1** (complexes **2** and **3** have very similar molecular structures; see Figures S1 and S2 in the Supporting Information). For all three complexes, two centrosymmetrically related Cu^{II} centres are bridged by azide ions in an asymmetric end-on fashion leading to relatively small $Cu\cdots Cu$ distances (Table 1). Within these dimeric units, each of the two trigonally distorted square pyramidal copper(II) centres is coordinated equatorially by three ligating atoms [O(1), N(1) and N(2)] of the corresponding tridentate Schiff-base ligand and a nitrogen atom, N(11), of one of the bridging azides; this comprises the basal plane. A second nitrogen atom, N(11)', from the centrosymmetrically related bridging azide coordinates axially at a rather long distance [$Cu-N(11)'$: $2.550(8)$, $2.447(6)$, $2.443(9)\text{ Å}$ for **1**, **2** and **3** respectively] furnishing

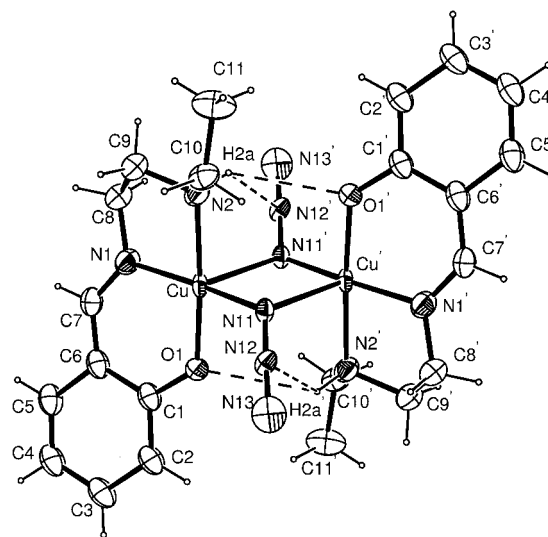


Figure 1. Ortep-3 view of complex **1** (30% thermal ellipsoids) with intramolecular hydrogen bonding (dashed line); atoms marked with a prime are transformed by the symmetry element $-x, 1-y, -z$

Table 1. Main structural and magnetic parameters for complexes **1**, **2** and **3**; parameters for complex **3b** are also included for comparison

Compound	Cu–Cu (Å)	Cu–azido (basal) (Å)	Cu–azido (apical) (Å)	Cu–N–Cu (°)	$\tau^{[a]}$	Angle N_3 –basal plane (°)	J_1 cm^{-1}
1	3.106	1.999	2.443	88.3	0.13	47.0	–2.63
2	3.232	1.985	2.447	93.0	0.23	39.0	–1.79
3	3.273	2.016	2.550	90.8	0.21	59.7	–5.37
3b ^[b]	3.318	2.060	2.475	93.6	0.26	57.2	–3.97
							+2.9

^[a] τ is the addition parameter.^[19] ^[b] Complex **3** in ref.^[18]

an elongated square-pyramidal (4+1) geometry for each copper(II) centre in all three complexes.

The four basal donor atoms [O(1), N(1), N(2) and N(11)] deviate from the mean coordination plane through them by 0.06(1), -0.10(1), 0.09(1) and -0.05(1) Å, respectively, in complex **1**, 0.08(1), -0.12(1), 0.12(1) and -0.13(1) Å, respectively, in complex **2**, and 0.11(1), -0.14(1), 0.16(1) and -0.12(1) Å, respectively, in complex **3**. The copper atom is slightly pulled out of this plane towards the apical donor atom N(11)' at a distance 0.125(1), 0.097(1) and 0.108(1) Å in complexes **1**, **2** and **3**, respectively. The distortions of the coordination polyhedron from the square pyramid to the trigonal bipyramid have been calculated by the Addison parameter (τ)^[19] as an indication of the degree of trigonality. τ is defined as $(\beta - \alpha)/60$, where β and α are the two trans-basal angles. For a perfectly square pyramidal geometry τ is equal to zero, while it becomes unity for a perfectly trigonal-bipyramidal geometry. The τ values for complexes **1**, **2** and **3** are 0.13, 0.23 and 0.21, respectively.

The five-membered chelate ring Cu–N1–C8–C9–N2 in complex **1** has a half-chair conformation, twisted around C(8)–C(9), with puckering parameters^[20] $q_2 = 0.383(16)$ Å and $\phi_2 = 54.4(2)^\circ$. The closest pucker^[21] conformation of the five-membered chelate rings Cu–N1–C4–C5–N2 in complexes **2** and **3** is an envelope on C(5); the puckering parameters^[20] are $q_2 = 0.426(6)$ Å and $\phi_2 = 115.3(7)^\circ$ in the former and $q_2 = 0.292(13)$ Å and $\phi_2 = 71.7(2)^\circ$ in the latter.

The bridging Cu₂N₂ network is exactly planar as dictated by symmetry. Due to the formation of basal-apical μ_2 -1,1-N₃ bridging, the bridging Cu–N bond lengths are significantly different ($\Delta d = 0.46$, 0.46 and 0.53 Å for **1**, **2** and **3**,

respectively). The bridging N₃[−] anions are quasi-linear; the N(11)–N(12)–N(13) angles are 177.5(15)°, 176.8 (7)° and 178.4 (10)° in **1**, **2** and **3**, respectively. The angles subtended at the metal in the coordination sphere are very similar in the three structures. There is, however, a significant difference between the Cu–N(11)–N(12) angles for the axial azide [122.3(9)° in **1**, 115.4(6)° in **2** and 131.9(6)° in **3**].

The three crystal structures exhibit different hydrogen-bonding patterns (Table 2). There is one hydrogen atom, H2a, in each of the complexes **1** and **2** available for hydrogen-bond formation, and two hydrogen atoms, H2a and H2b, in complex **3**. H2a in each of the three complexes is involved in strong intra-dimer N–H...O hydrogen bonding with the ligating oxygen O1 of the corresponding tridentate Schiff-base ligand (Figure 1 and Figures S1 and S2 in the Supporting Information). In addition, in complex **1** a second direct connection is established between the two

Table 2. Hydrogen-bonding distances (Å) and angles (°) for complexes **1**, **2** and **3**

Compound	D–H...A ^[a]	D–H	D...A	H...A	$\angle$ D–H...A
1	N2–H2a...O1 ⁱ	0.910	3.233(16)	2.612	126.1
	N2–H2a...N12 ⁱ	0.910	3.249(16)	2.622	126.7
	N2–H2a...N13 ⁱⁱ	0.910	3.533(19)	2.900	127.9
2	N2–H2a...O1 ⁱⁱⁱ	0.910	3.221(8)	2.371	155.5
3	N2–H2a...O1 ^{iv}	0.901	3.260(12)	2.452	149.4
	N2–H2b...N11 ^v	0.899	3.285(13)	2.673	126.2

^[a] Symmetry operations for generating equivalent atoms: i) $-x, 1 - y, -z$; ii) $1 + x, y, z$; iii) $-x, -y, 1 - z$; iv) $1 - x, 1 - y, 1 - z$; v) $2 - x, 1 - y, 1 - z$.

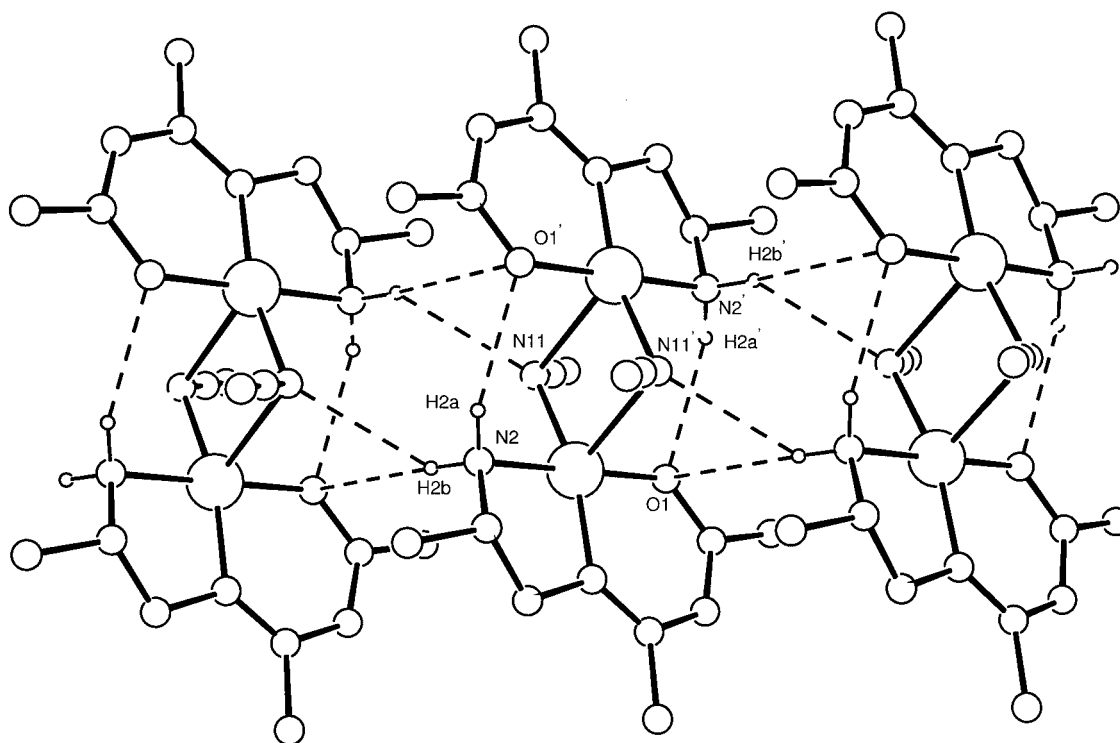


Figure 2. Scheme of the packing (one-dimensional) in complex **3**; the intermolecular hydrogen bonds (magnetic pathways) are shown as dashed lines; atoms marked with a prime are transformed by the symmetry element $1 - x, 1 - y, 1 - z$

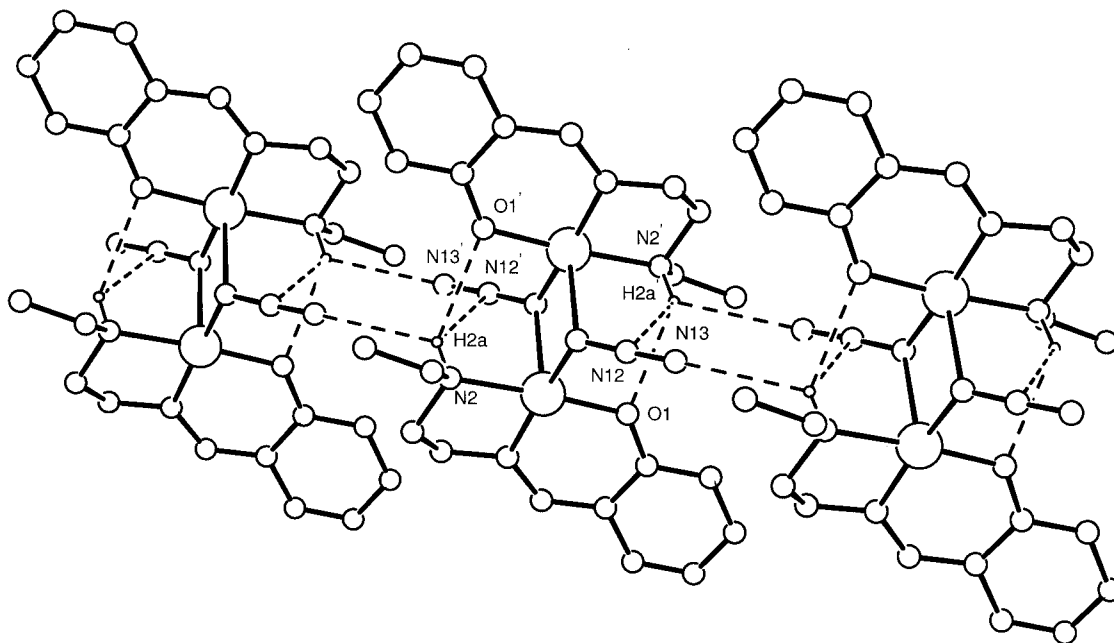


Figure 3. Scheme of the packing (one-dimensional) in complex **1**; the intermolecular hydrogen bonds (magnetic pathways) are shown as dashed lines; atoms marked with a prime are transformed by the symmetry element $-x, 1-y, -z$

halves of the dinuclear entity through strong intra-dimer N–H $\cdots$ N hydrogen bonding with the middle centrosymmetrically related bridging azido nitrogen N12 (Figure 1).

The inter-dimer interaction is significantly different in complexes **1**, **2** and **3** (Table 2). H2b in complex **3** bridges the symmetry-related dimers through an N2–H2b $\cdots$ N11 [N2 $\cdots$ N11:3.285(13) Å] hydrogen bond in a one-dimensional supramolecular entity (Figure 2). H2a in complex **1** is similarly involved in a somewhat weaker N2–H2a $\cdots$ N13 [N2 $\cdots$ N13:3.533(19) Å] hydrogen bond-like contact with a neighbouring dimer (Figure 3). Complex **2** does not show any important intermolecular hydrogen bond in the “one-dimensional” net.

Magnetic Properties

Before reporting the experimental data, it is important to underline which are the magnetic pathways in the three complexes, according to the structural data discussed above. Complex **1** can be considered as a dinuclear complex in which the Cu ions are linked by two azido bridging ligands in an end-on equatorial-apical fashion (μ -1,1) through the N11 atom. There are also two short intramolecular hydrogen bonds [O1–H2a(N2): 2.613 Å; N12–H2a(N2): 2.621 Å]. The same H2a(N2) is linked by a weak, hydrogen bond-like contact to N13 (terminal nitrogen of the azido bridging ligand) of another dinuclear complex at 2.934 Å, thus giving a pseudo-one-dimensional supramolecular entity (Figure 3). Complex **2** shows the same intramolecular pathway [Cu–(μ -1,1-N₃)₂–Cu]. There is also a short intramolecular hydrogen bond [O1–H2a(N2): 2.37 Å], but in this case there is no appreciable hydrogen bond between adjacent dimers. The shortest H2a(N2) distances are 5.5 Å to N11 and 6.13 Å to O1 of a neighbouring dinuclear entity. Thus, com-

plex **2** can be considered as an isolated dinuclear complex. Complex **3** shows the same intramolecular pathway [Cu–(μ -1,1-N₃)₂–Cu] through the N11 atom. There is also a short intramolecular hydrogen bond [O1–H2a(N2): 2.452 Å]. The H2b(N2) atom is linked by a weak hydrogen bond to N11 (first nitrogen of the azido bridging ligand) of another dinuclear complex at 2.673 Å, thus giving a pseudo-one-dimensional supramolecular entity (Figure 2). In this one-dimensional structure H2b(N2) links the O1 of an adjacent unit at 3.063 Å, with H2a $\cdots$ H2a at 3.091 Å and H2a $\cdots$ H2b at 3.323 Å.

Complexes 1 and 2

The magnetic properties of complexes **1** and **2** are very simple and correspond to almost isolated dinuclear entities from the magnetic point of view, at least down to 2 K. A $\chi_m T$ versus T plot (χ_m is the molar magnetic susceptibility for two Cu^{II} ions) for complex **1** is shown in Figure 4 [for the analogous complex **2** the corresponding figure is given in the Supporting Information (Figure S3)]. The value of $\chi_m T$ for **1** at 300 K is 0.83 cm³·mol^{−1}·K, which is as expected for two magnetically quasi-isolated spin doublets ($g > 2.00$). The $\chi_m T$ values decrease smoothly from 0.83 to 0.35 cm³·mol^{−1}·K at 2 K. This global feature is characteristic of very weak antiferromagnetic coupling. Considering the possible interactions through the dinuclear entities as nil, the Bleaney–Bowers formula for a dinuclear $S = 1/2$ system was used.^[22] The Hamiltonian employed is $H = -JS_1S_2$. The best-fit parameters were: $J = -2.63 \pm 0.01$ cm^{−1}, $g = 2.11$ and $R = 2.1 \times 10^{-5}$ for **1** and $J = -1.79 \pm 0.01$ cm^{−1}, $g = 2.13$ and $R = 12.1 \times 10^{-5}$ for **2** (R is the agreement factor defined as $\sum_i [(\chi_m T)_{\text{obsd.}} - (\chi_m T)_{\text{calcd.}}]^2 / \sum_i [(\chi_m T)_{\text{obsd.}}]$, the temperature-independent paramagnetism

(TIP) was taken as $120 \times 10^{-6} \text{ cm}^3 \cdot \text{mol}^{-1}$ }.^[22b] All attempts to improve the fits by introducing a small percentage of mononuclear impurities or a possible intermolecular J' (molecular-field approximation) did not improve the R values, and the intramolecular J values were left unmodified. The reduced molar magnetisation tends to $1.7 N\beta$ for both **1** and **2** when the fields approach 5 T (see inset in Figure 4 and Figure S3), and they do not follow the de Brillouin formula for two isolated Cu^{II} ions. This feature is also indicative of the small antiferromagnetic coupling in both compounds.

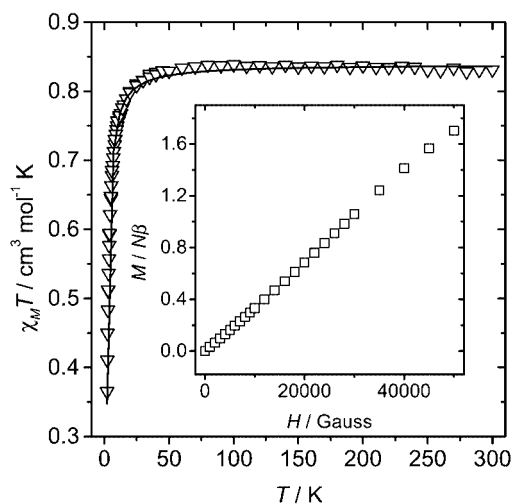


Figure 4. Plot of $\chi_m T$ vs. T for complex **1**; the solid lines represent the best fit and the points the experimental data; inset: plot of $M/N\beta$ vs. H at 2 K for complex **1**

Complex 3

The magnetic properties of complex **3** are different from those of complexes **1** and **2**. The $\chi_m T$ versus T plot (χ_m is the molar magnetic susceptibility for two Cu^{II} ions) is shown in Figure 5. The value of $\chi_m T$ at 300 K is $0.85 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$, which is as expected for two magnetically quasi-isolated spin doublets ($g > 2.00$). The $\chi_m T$ values smoothly decrease from 0.85 to $0.1 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ at 2 K. The global feature is characteristic of weak antiferromagnetic coupling. Considering the possible interactions through the dinuclear entities as nil, all attempts to fit the experimental data with only one $J_{\text{intramolecular}}$ value were unsuccessful.^[22] The J value was of the order of $4\text{--}5 \text{ cm}^{-1}$ but with an unsatisfactory R value. As indicated above, complex **3** is a one-dimensional system formed by dinuclear entities linked by hydrogen bonds. This gives an alternating $S = 1/2$ system (J_1 for azido bridging ligand and J_2 for hydrogen bond). The fit of the magnetic data has been carried out with the Clumag program using a ring of twelve copper(II) ions which is the best way to represent the infinite character of the chain.^[23] The best-fit parameters obtained with this computing model are: $J_1 = -5.37 \pm 0.06 \text{ cm}^{-1}$, $J_2 = -3.97 \pm 0.08 \text{ cm}^{-1}$, $g = 2.14$ and $R = 0.5 \times 10^{-5}$ (TIP was taken as $60 \times 10^{-6} \text{ cm}^3 \cdot \text{mol}^{-1}$ for the copper ion).^[22b] The reduced molar magnetisation (see inset in Fig-

ure 5) clearly indicates that the global coupling is more antiferromagnetic than that for complexes **1** and **2**. For **3** the $M/N\beta$ value at 5 T tends to $0.7 N\beta$, which is very far from the expected value for two isolated copper(II) ions. The shape of the curve formed by the experimental point does not follow the de Brillouin formula, and its convexity is more pronounced than in **1** and **2**. Thus, the global antiferromagnetic coupling is greater than for **1** and **2**.

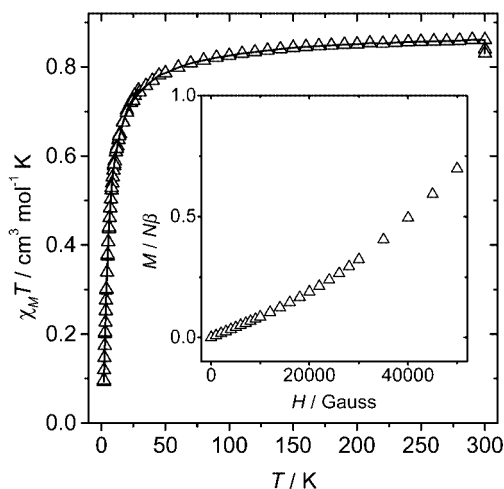


Figure 5. Plot of $\chi_m T$ vs. T for complex **3**; the solid lines represent the best fit and the points the experimental data; inset: plot of the $M/N\beta$ vs. H at 2 K for complex **3**

Magneto-Structural Correlations

Intramolecular Interactions (J_1) through End-On Azido Bridging Ligands

Complexes **1**, **2** and **3** show antiferromagnetic coupling. For complex **3** it is impossible to state if the J value for the azido bridging ligand is -5.38 cm^{-1} or -3.97 cm^{-1} but it seems logical to assume that the intramolecular azido coupling would be greater than the intermolecular hydrogen-bond coupling. In any case both are negative and of the same order of magnitude. When the azido bridge is in a basal-basal position, either the experimental values or the theoretical calculations demonstrate that J can be antiferromagnetic or ferromagnetic depending mainly on the $\text{Cu-N}_3\text{-Cu}$ angle.^[17] This reasoning is not valid when the azido bridges are in basal-apical coordination (such as in **1**, **2** and **3**), although too many papers devoted to this kind of coupling try to relate this angle with the J parameter. The literature data indicate a total dispersion of the J values with regard to the Cu-N-Cu angles.^[6–16,18] In equatorial-axial complexes (such as in **1**, **2** and **3**), the distortion parameter τ (square-pyramidal to trigonal bipyramidal)^[19] could be important from a magnetic point of view. However, experimentally, the maximum value of τ gives, surprisingly, the minimum value of J . The variations in J are small and, consequently, it would be difficult to establish clear trends connecting theoretical parameters to variations in J .

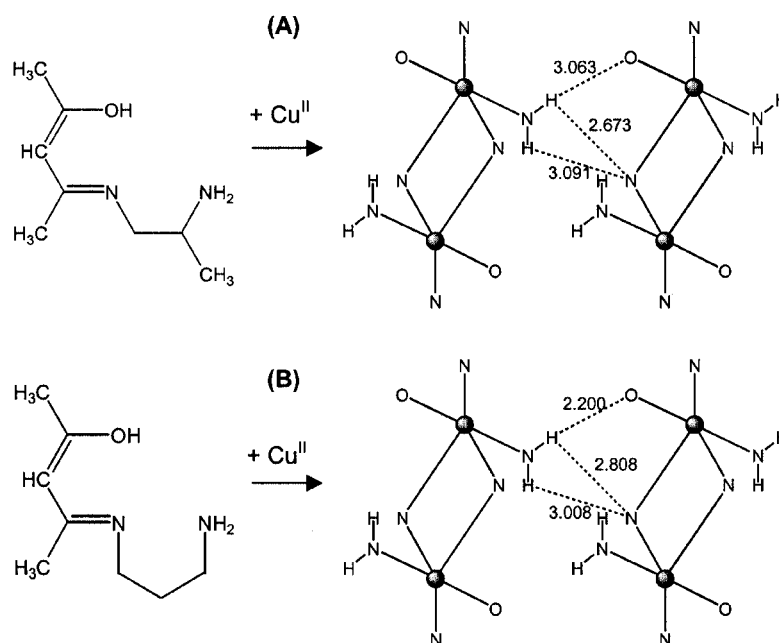


Figure 6. Scheme of the ligands and complex **3** (A) (antiferromagnetically coupled) and complex reported by the authors in ref.^[18] (B) (ferromagnetically coupled)

The main structural parameters for the three complexes are gathered in Table 1.

Intermolecular Hydrogen Bonds in Complex **3** – Small Subtleties That Modify the Magnetism

It is well known that the role played by hydrogen bonds in the transmission of magnetic interactions is still not fully understood. For many years, hydrogen bonds were thought to propagate essentially antiferromagnetic interactions between metal centres,^[3] but the number of ferromagnetically coupled hydrogen-bonded systems is growing.^[1a,4] We decided to compare two very similar complexes, complex **3** and the other one previously reported by us;^[18] the ligands and their main structural parameters are schematized in Figure 6. Although the ligands are very similar and the packing of the two complexes is analogous, subtle differences can be found: in **3** the shorter intermolecular hydrogen bond length is N–H $\cdots$ N(azido) (rather long) while in the previous complex,^[18] the stronger hydrogen-bond length is N–H $\cdots$ O (very short). The experimental result is that complex **3** clearly shows intermolecular antiferromagnetic coupling while its analogue shows intermolecular ferromagnetic coupling.^[18] Although J_{inter} is large, close to -4 cm^{-1} (see above), other much greater J values are reported in literature, such as $J = -90 \text{ cm}^{-1}$ (Cu dimer with O–H $\cdots$ O distance of $2.32 \text{ \AA}$).^[24] Even for other metals, like chromium(III), considerable large J values are also reported.^[3a,25]

Concluding Remarks

Three very similar blocking ligands have been used to synthesise three new, basal-apical, end-on azide-bridged, di-

nuclear Cu^{II} complexes. The dinuclear entities of all three complexes are very similar but the H-bonding network among the dinuclear entities and consequently their relative orientation in the one dimensional net are very different. From a magnetic point of view, it is important to emphasise that for basal-apical coordination neither the Cu–N–Cu angle nor the τ distortions are clearly indicative of the magnetic interaction.

The difference between the antiferromagnetic character (intra and inter) in **3** with regard to the ferromagnetic character in its homologue^[18] is a challenge for experimental and theoretical chemists to synthesise new similar complexes and to try to interpret the subtle differences that cause the drastic change in the magnetic behaviour.

Experimental Section

Caution! Azido complexes of metal perchlorates in the presence of organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with care.

Physical Measurements: Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin–Elmer 240C elemental analyzer and the copper contents in all the complexes were estimated spectrophotometrically.^[26] IR spectra of the complexes in KBr ($4500\text{--}500 \text{ cm}^{-1}$) were recorded using a Perkin–Elmer RXI FT-IR spectrophotometer. Electronic spectra of the complexes in methanol ($1200\text{--}350 \text{ nm}$) were recorded on a Hitachi U-3501 spectrophotometer. The crystallographic data of complex **1** were collected on a Bruker Nonius MACH3 diffractometer and for complexes **2** and **3** were collected on a MARResearch Image Plate system. Magnetic measurements were carried out in the “Servei de Magnetoquímica (Universitat de Barcelona)” on polycrystalline samples (30 mg) with a Quantum Design MPMS XL-5 SQUID susceptometer operating

at a magnetic field of 0.1 T between 2 and 300 K. The diamagnetic corrections were evaluated from Pascal's constants.

Materials: All the chemicals were of reagent grade and used without further purification. The three monocondensed ligands were synthesised as described below.

Preparation of HL¹ {N-[2-Ethylamino]ethyl}salicylaldimine} and HL² (7-Ethylamino-4-methyl-5-azahept-3-en-2-one): Both HL¹ and HL² were prepared by condensation of the NH₂ group of *N*-ethyl-1,2-ethanediamine (0.45 mL, 5 mmol) with salicylaldehyde (0.53 mL, 5 mmol) and 2,4-pentanedione (0.55 mL, 5 mmol), respectively, in methanol (30 mL) under reflux for 3 h.

Preparation of 7-Amino-4-methyl-5-azaoc-3-en-2-one (HL³): This ligand was prepared by following a similar method to that adopted for the half condensation of 1,2-ethanediamine or 1,3-propanediamine with 2,4-pentanedione as reported earlier.^[27] A solution of 2,4-pentanedione (1.1 mL, 10 mmol) in chloroform (50 mL) was added dropwise to a solution of 1,2-propanediamine (0.80 mL, 10 mmol) in chloroform (50 mL) at ambient temperature. After completion of the addition, the solution was stirred for an additional 3 h and the chloroform was then evaporated under reduced pressure. The resultant viscous oil was collected and dissolved in methanol (30 mL).

Synthesis of [CuL¹N₃]₂ (1), [CuL²N₃]₂ (2) and [CuL³N₃]₂ (3): Direct synthesis of the complexes from methanolic solutions of Cu(ClO₄)₂·6H₂O, NaN₃ and the respective ligands did not allow the formation of sufficiently pure desired products. A mixture of hydrolysed products as well as a small amount of the respective complexes was formed. It was very difficult to separate the mixture. Therefore, to prepare good quality crystalline compounds, we adopted the following procedure.

Addition of copper(II) perchlorate hexahydrate to a methanolic solution of HL¹, HL² or HL³, followed by addition of a stoichiometric amount of triethylamine, gave the dinuclear complex [(CuL¹)₂](ClO₄)₂ and the trinuclear complexes [(CuL²)₃(OH)]-(ClO₄)₂·H₂O and [(CuL³)₃(OH)](ClO₄)₂, respectively, as reported previously for similar compounds.^[28]

A methanol/water solution (9:1, v/v) of sodium azide, (0.13 g, 2 mmol) was added to a methanolic solution (30 mL) of [(CuL¹)₂]-

(ClO₄)₂ (0.35 g, 0.5 mmol), [(CuL²)₃(OH)](ClO₄)₂·H₂O (0.47 g, 0.5 mmol) or [(CuL³)₃(OH)](ClO₄)₂ (0.44 g, 0.5 mmol) and the mixture was stirred for 30 min. There was no immediate separation of any compounds. The clear solutions were therefore left to stand in a refrigerator overnight. Dark-green plate-shaped single crystals of **1** and blue parallelepiped-shaped single crystals of **2** and **3** suitable for X-ray diffraction were obtained.

Complex 1: Yield: 0.20 g (65%). C₂₂H₃₀N₁₀O₂ (593.66): calcd. C 44.5, H 5.1, N 23.6, Cu 21.4; found C 44.5, H 5.2, N 23.7, Cu 21.1. UV/Vis (methanol): λ_{max} (ε_{max}) = 613 nm (287 dm³·mol⁻¹·cm⁻¹). IR: 3239 cm⁻¹ ν(N–H); 1630 ν(C=N).

Complex 2: Yield: 0.35 g (80%). C₁₈H₃₄N₁₀O₂ (549.65): calcd. C 39.3, H 6.2, N 25.5, Cu 23.1; found C 39.2, H 6.0, N 25.6, Cu 22.8. UV/Vis (methanol): λ_{max} (ε_{max}) = 595 nm (334 dm³·mol⁻¹·cm⁻¹). IR: 3241 cm⁻¹ ν(N–H); 1594 ν(C=N).

Complex 3: Yield: 0.27 g (70%). C₁₆H₃₀N₁₀O₂ (521.60): calcd. C 36.8, H 5.8, N 26.8, Cu 24.3; found C 36.7, H 5.9, N 26.7, Cu 24.0. UV/Vis (methanol): λ_{max} (ε_{max}) = 591 nm (226 dm³·mol⁻¹·cm⁻¹). IR: 3245 and 3292 cm⁻¹ ν(N–H); 1592 ν(C=N).

Crystallographic Studies: The crystallographic data of complex **1** were collected on a Bruker-Nonius MACH3 diffractometer using the ω-2θ scan mode in the θ range 2–25°; a maximum of 60 s were allowed per reflection. The data for complexes **2** and **3** were collected on a MAResearch Image Plate System with the crystals positioned at 70 mm from the plate; 100 frames were measured at 2° intervals with a counting time of 2 min per frame. Mo-K_α radiation was used in all three cases.

The raw intensity data for complex **1** were processed for Lorentz and polarisation effects using the XCAD4 program in the WinGX suite and empirical absorption correction was carried out using ψ-scan data.^[29] The data for complexes **2** and **3** were processed using the XDS^[30] program and empirical absorption corrections were applied using DIFABS.^[31] The number of independent reflections for complexes **1**, **2** and **3** were 2119, 2174 and 1940, respectively.

The structures were solved by direct methods with the SHELXS-97 program.^[32] Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon and nitrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2-times those of the atom to which they are attached. The crystals of **3** were twinned (*hkl*, *hk*–*l*)

Table 3. Selected crystal parameters, data collection and structure refinement of complexes **1**, **2** and **3**

	1	2	3
Formula	C ₂₂ H ₃₀ N ₁₀ O ₂ Cu ₂	C ₁₈ H ₃₄ N ₁₀ O ₂ Cu ₂	C ₁₆ H ₃₀ N ₁₀ O ₂ Cu ₂
<i>F</i> _w	593.66	549.65	521.60
<i>T</i> (K)	293	293	293
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
Wavelength (Å)	0.70930	0.71073	0.71073
<i>a</i> (Å)	8.390(2)	8.070(9)	5.884(7)
<i>b</i> (Å)	7.512(2)	9.787 (12)	16.147(18)
<i>c</i> (Å)	19.822(6)	15.743(17)	11.901(12)
Crystal system	monoclinic	monoclinic	monoclinic
<i>α</i> (°)	90	90	90
<i>β</i> (°)	91.45(5)	98.467(10)	90.050(10)
<i>γ</i> (°)	90	90	90
<i>V</i> (Å ³)	1248.9(6)	1230(2)	1131(2)
<i>Z</i>	2	2	2
<i>D</i> _{calcd.} (g/cm ³)	1.579	1.484	1.532
<i>μ</i> (mm ⁻¹)	1.7	1.8	1.9
<i>F</i> (000)	612	572	540
<i>R</i> int [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.1193 <i>wR</i> 2 = 0.2855	<i>R</i> 1 = 0.0767 <i>wR</i> 2 = 0.1469	<i>R</i> 1 = 0.0852 <i>wR</i> 2 = 0.2145

Table 4. Selected bond lengths (Å) and angles (°) for complexes **1**, **2** and **3**

	1	2	3
Cu–O1	1.891(10)	1.929(5)	1.913(8)
Cu–N1	1.950(12)	1.933(5)	1.944(8)
Cu–N2	2.040(12)	2.032(5)	1.994(8)
Cu–N11	1.988(10)	1.985(6)	2.016(8)
Cu–N11S1' ^[a]	2.443(9)	2.447(6)	2.550(8)
O1–Cu–N1	93.6(5)	94.7(2)	94.6(3)
O1–Cu–N2	176.2(5)	179.8(2)	178.1(3)
O1–Cu–N11	88.8(4)	90.6(2)	89.9(3)
O1–Cu–N11S1'	95.1(4)	92.4(2)	90.1(3)
N1–Cu–N2	83.9(5)	85.5(2)	84.6(4)
N1–Cu–N11	168.1(5)	166.0(2)	165.5(3)
N1–Cu–N11S1'	99.7(5)	105.7(2)	104.5(3)
N2–Cu–N11	93.1(4)	89.2(2)	91.3(3)
N2–Cu–N11S1'	88.2(4)	87.4(2)	88.4(3)
N11–Cu–N11S1'	91.7(4)	87.0(2)	89.2(3)
Cu–N11–CuS1'	88.3(4)	93.0(2)	90.8(3)

^[a] Symmetry elements S1': $-x, 1-y, -z$ for complex **1**; $-x, -y, 1-z$ for complex **2**; $1-x, 1-y, 1-z$ for Complex **3**.

with a refined ratio of 3:1. The structures were refined on $I (=|F|^2)$ using SHELXL-97^[33] to $R1$ 0.1193, $wR2$ 0.2855 using 1281 reflections for complex **1**, $R1$ 0.0767, $wR2$ 0.1405 using 1880 reflections for complex **2**, and $R1$ 0.0852, $wR2$ 0.2042, using 1521 reflections for complex **3**. Reflections with $I > 2\sigma(I)$ were considered to be "observed". The relatively high residuals for complex **1** can be attributed to the rather flaky nature of the crystals, which prevented accurate data collection. The crystal structure illustrations were generated using ORTEP-3.^[34] The crystallographic data are summarised in Table 3; selected interatomic distances and angles are presented in Table 4.

CCDC-227085 (for **1**), -227086 (for **2**) and -227087 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-(0)1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

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