A Binuclear Copper(II) Acetate Complex Showing a 3D Supramolecular Network with Hydrophilic Pockets: Its Unusual Magnetic Behaviour

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The binuclear complex [Cu$_2$L(OAc)]·6H$_2$O (**1**) {H$_3$L = 2-(2-hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine} which shows an unusual magnetic superexchange behaviour, acts as a building block for a novel three-dimensional metal-organic framework, with hydrophilic pockets.

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Introduction

Coordination complexes that define unusual network topologies have attracted special interest not only because of their intriguing architectures, but also of their tremendous potential applications in a wide number of fields.[1−7] However, the assembly of inorganic materials from organic ligands and metal-ion building blocks to generate new supramolecular architectures is still a challenge. Supramolecular inorganic/organic hybrid materials have so far been constructed through two principal design philosophies. The most common approach is the assembly of transition metal complexes into coordination polymers using coordinative covalent bonds.[2−6,8−11] The second method makes use of weaker intermolecular forces (particularly π-π interactions and hydrogen bonding)[7,12−15] for connecting building blocks into a wide variety of extended networks.

In this work, a novel case of "one-pot" self-assembled 3D networks, by combination of coordinative and intermolecular interactions, with brick-wall shaped channels, is described (Figure 1). This topology has not been previously reported to the best of our knowledge. The binuclear copper complex, which acts as building block, shows an unfamiliar superexchange pathway, with a net ferromagnetic behaviour.

Results and Discussion

The reaction of 2-(2-hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine (H$_3$L)[16]

with copper(II) acetate dihydrate in methanol/acetonitrile yields a deep green solution in air. Its slow evaporation leads to the isolation of crystals of [Cu$_2$L(OAc)]·6H$_2$O (**1**), suitable for X-ray diffraction studies.

The crystal structure shows that **1** consists of binuclear [Cu$_2$L(OAc)] units (Figure 2) with water molecules as solvates. The isolated units contain both copper atoms doubly bridged by a phenolate oxygen atom [O(103)] of the central ligand arm and by an oxygen atom from an acetate ligand [O(11)]. This gives rise to an intramolecular Cu(11)···Cu(12) separation of 3.1450(19) Å. The Cu−O distances [Cu(11)−O(103) and Cu(12)−O(103); Cu(11)−O(11) and Cu(12)−O(11)] reflect the asymmetry of both endogenous and exogenous bridges. The Cu(11)−O(103)−Cu(12) and Cu(11)−O(11)−Cu(12) bridging angles are 102.5(2)° and 91.8(2)° respectively. The geometry around both copper atoms can be described as highly distorted square pyramidal (τ = 0.43 and 0.35 for Cu(11) and Cu(12) respectively), with O(11) at the apex of both pyramids. As a result, the complex consists of two distorted square pyramids sharing one base-to-apex edge (Scheme 1, Type I). The distorted basal planes form an angle of 133.9°. Two other types of arrangements are described in the literature for square-pyramidal complexes containing a Cu$_2$O$_2$ core: a) square pyramids sharing one base-to-apex edge but with parallel basal planes (Scheme 1, Type II); b) square pyramids sharing one basal edge with coplanar basal planes (Scheme 1, Type III). To the best of our knowledge, the situation Type I has not been previously reported for this kind of complex. In addition, the nearly perpendicular orientation of the Cu−Oph−Cu ideal plane and the central phenyl ring (90.6°) is remarkable.

The [Cu$_2$L(OAc)] units form an extended array by a combination of π···π, CH···π and C−H···O hydrogen bonds,[17] leading to the formation of a 3D network with hydrophilic channels along the (001) direction of ca. 11 × 7 Å^2 (Fig-

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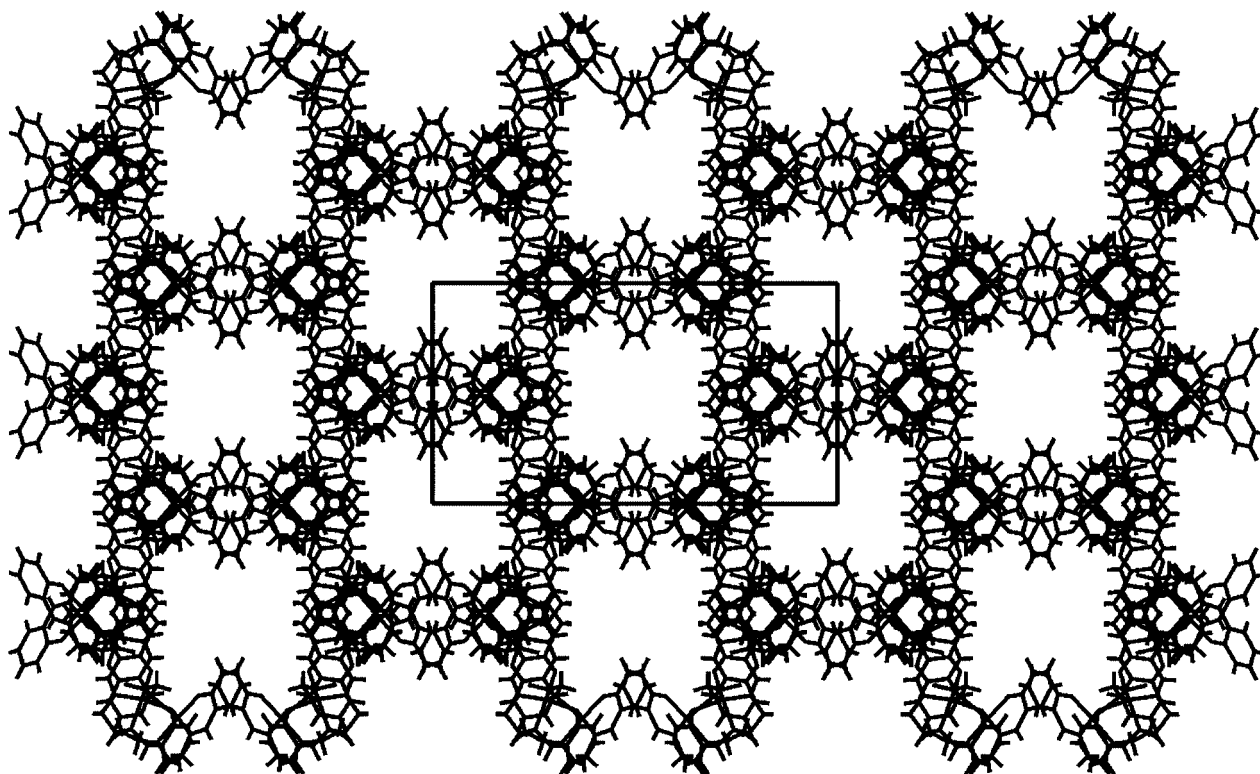48080 Bilbao, Spain

Figure 1. View of the packing of **1** along the (001) direction; guest water molecules are omitted for clarity
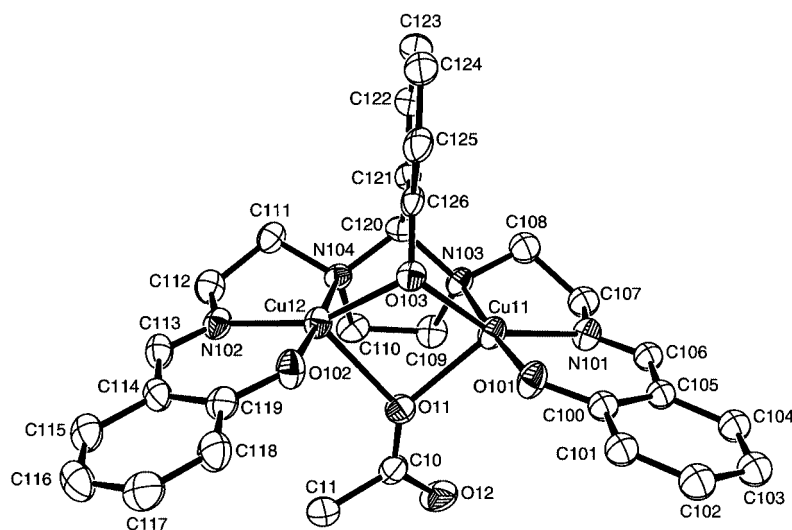

Figure 2. An ORTEP view of **1** showing 30% probability thermal ellipsoids (water molecules and hydrogen atoms are omitted for clarity); selected bond lengths and angles: Cu(11)−O(101) 1.909(6), Cu(11)−N(101) 1.950(7), Cu(11)−O(103) 2.042(6), Cu(11)−N(103) 2.076(7), Cu(11)−O(11) 2.171(6), Cu(12)−O(102) 1.919(6), Cu(12)−N(102) 1.931(7), Cu(12)−O(103) 1.991(5), Cu(12)−N(104) 2.076(7), Cu(12)−O(11) 2.208(6); O(101)−Cu(11)−N(103) 175.4(3), N(101)−Cu(11)−O(103) 149.5(3), N(101)−Cu(11)−O(11) 130.4(3), O(103)−Cu(11)−O(11) 79.5(2), O(102)−Cu(12)−N(104) 176.3(3), N(102)−Cu(12)−O(103) 155.2(3), N(102)−Cu(12)−O(11) 124.2(3), O(103)−Cu(12)−O(11) 79.7(2)

ure 1). Thus, the total void space, neglecting the solvent molecules, represents 34.2% of the cell volume. The water molecules occupy most of the void space and form an intricate hydrogen bond scheme. According to the structural data, they can be roughly assigned as: a) tightly bonded molecules, anchored to the network by one or more hydrogen bonds involving the phenol oxygen atoms or the unco-

ordinated acetate oxygen atom (O1w, O2w, O4w, O5w); b) loosely bonded molecules showing only contacts with other water molecules (the remaining solvent molecules).

ESR spectra for the title compound were recorded on powdered samples in the temperature ranges 4.2−300 K and 100−300 K operating at X- and Q-bands, respectively. Despite the extremely large observed signals, the spectrum

Type I

Type II   Type III
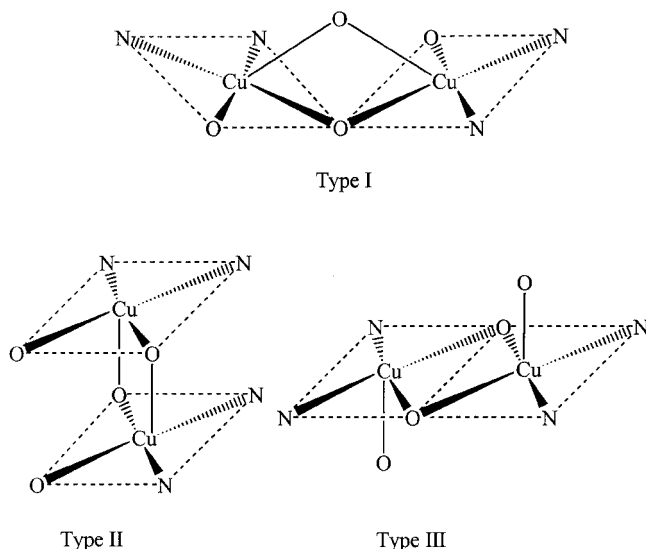
Scheme 1. Square pyramidal arrangements for Cu_2O_2 containing complexes

obviously corresponds to an $S = 1$ triplet state, as expected for an isolated binuclear Cu^{II} complex, with important zero-field splitting. The existence of a triplet state is confirmed by the presence of a "half-field" signal ($\Delta M_s = \pm 2$) in both X- and Q-band spectra. Unfortunately, the poor resolution of the spectra has precluded any unambiguous determination of the main components of the g and D tensors.

Magnetic susceptibility measurements have been performed between 5 and 300 K. Figure 3 shows the thermal evolution of the magnetic molar susceptibility, together with a plot of $\chi_m T$ vs T ($\chi_m T = \mu_{eff}^2/8$). Above 100 K, the data are well described by a Curie−Weiss law ($\chi_m = C_m/T-\theta$), with $C_m = 0.86$ cm³ K/mol and $\theta = +12.6$ K. The positive θ value, as well as the overall appearance of the $\chi_m T$ vs. T curve, are indicative of the predominance of ferromagnetic interactions in this compound. The $\chi_m T$ product increases from 0.89 cm³K/mol at room temperature to 1.13 cm³K/mol at 5 K.

Taking into account the crystal structure of this compound, the susceptibility data have been fitted to the Bleaney−Bowers equation[18] derived from the Heisenberg
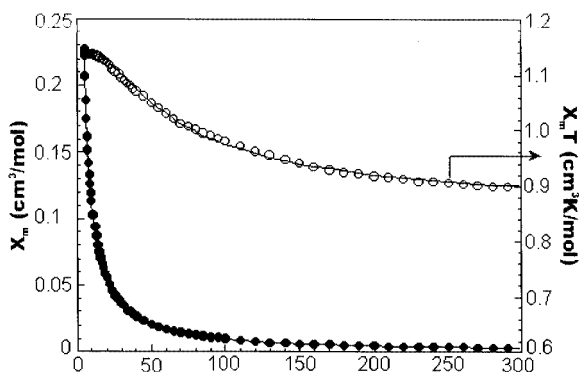
spin Hamiltonian ($H = -2JS_1S_2$) for two coupled $S = 1/2$ ions:

$$\chi_m = \frac{2Ng^2\beta^2}{kT}\left[\frac{1}{3+\exp(-2J/kT)}\right] \tag{1}$$

The best least-squares fit (solid lines in Figure 3) is obtained with the parameter $2J = +49.2$ cm⁻¹ ($J/k = +35.4$ K) and $g = 2.13$. Attempts to evaluate the possible interbinuclear interactions by means of a J' parameter treated in the molecular field approximation, led to extremely low values without any significant improvement of the fit.

As the geometry around both copper atoms is distorted square pyramidal, the $d_{x^2-y^2}$ magnetic orbitals (containing the unpaired electron) point towards the bridging phenolate oxygen atom. Therefore, the structure of complex **1** suggests that O(103) provides the likely pathway for coupling. The bridging acetate oxygen atom is at the common apical position of the square pyramidal chromophores, indicating that O(11) does not participate or shows negligible contribution to the superexchange pathway. Therefore, the magnetic behaviour of this complex is rather unusual. The main superexchange pathway is a phenolate oxygen atom, and binuclear copper complexes that share just one basal phenolate oxygen atom are usually antiferromagnetic.[19−23] In fact, just one binuclear copper of this type, which shows a square pyramidal arrangement of Type II, is described to be weakly ferromagnetic.[24] Besides, doubly bridged phenolate copper complexes usually show strong antiferromagnetic coupling.[25−29] The ferromagnetic behaviour of complex **1** can be attributed to its unusual structural features, detailed above.

In summary, this study reports the first complex containing a Cu_2O_2 core with a Type I arrangement, which shows an unfamiliar magnetic behaviour. Complex **1** acts as a building block to produce a 3D framework via weak intermolecular interactions. The network shows brick-wall shaped hydrophilic channels with unprecedented topology.

Experimental Section

Synthesis of 1: A solution of copper acetate dihydrate (0.25 g, 1.25 mmol) in methanol (30 mL) was mixed with a solution of H_3L (0.287 g, 6.23 mmol) in acetonitrile (30 mL). The resultant green solution was stirred at room temperature for 4 h. Slow evaporation of the solution yielded crystals of **1** (Yield: 0.35 g, 74.6%). $C_{29}H_{42}Cu_2N_4O_{11}$ (749.75): calcd. C 46.5, H 5.6, N 7.5; found C 46.9, H 5.7, N 7.2. (KBr): ν(C=N) = 1634 cm⁻¹ (s). ES-MS: $m/z = 581.1$ [Cu_2L^+].

X-ray Crystallography: Prism-shaped green crystals of **1** were grown as detailed above. Data were collected on a Smart-CCD-

Figure 3. Magnetic data for **1** at 5−300 K

1000 BRUKER diffractometer, using graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å), operating at room temperature. The structure was solved by direct methods and refined by full-matrix least-squares based on F^2 using the SHELX-97 program package.[30] Absorption correction was carried out semi-empirically from equivalents using the SADABS program.[31] Crystal data: $C_{29}H_{42}Cu_2N_4O_{11}$, $M_r = 749.75$ g·mol^{-1}, monoclinic, space group $C2/c$, $a = 31.831(11)$, $b = 13.968(5)$, $c = 20.754(7)$ Å, $\beta = 126.359(19)°$, $V = 7431(4)$ Å^3, $Z = 8$, $D_c = 1.340$ Mg·m^{-3}, $F(000) = 3120$, $\mu(Mo\text{-}K_\alpha) = 1.201$ mm^{-1}. 5367 Unique reflections were measured. Final $R1 = 0.1480$ on all data, conventional $R1 = 0.0661$ on $[I > 2\sigma(I)]$.

CCDC-205980 contains 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: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

EPR and Magnetic Measurements: A Bruker ESP300 spectrometer, operating at X- and Q-bands and equipped with standard Oxford low temperature devices, was used to record the ESR powder spectra of **1** at different temperatures. The magnetic field was calibrated by an NMR probe and the frequency inside the cavities was determined with a Hewlett−Packard 5352B microwave frequency counter. Magnetic susceptibility measurements were performed on powdered samples between 5 and 300 K with a Quantum Design MPMS-7 SQUID magnetometer. The magnetic field used in the experiments was 0.1 T, a value at which the magnetisation versus magnetic field curve was still linear at 5 K. Experimental susceptibility values were corrected for diamagnetic contributions and for temperature-independent paramagnetism.

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