

Ferromagnetic Coupling in Copper(II) [2 × 2] Grid-like Complexes

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Supporting Information

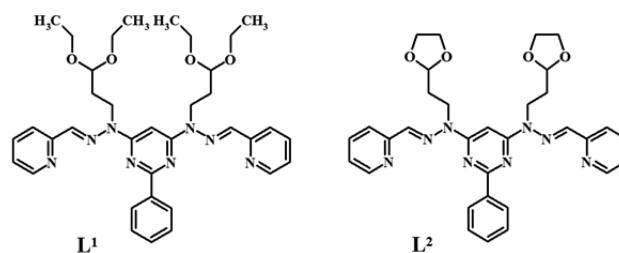
ABSTRACT: Two copper(II) [2 × 2] grid-like complexes were synthesized and structurally characterized. Investigation of the magnetic properties showed for both the occurrence of intramolecular ferromagnetic interactions.

The self-assembly processes of specific metallocupramolecular architectures from a set of organic ligands and metal ions result from the correct reading of the structural information stored within the ligands by the metal ions operating through a coordination algorithm.¹ Among these systems, grid-type arrangements attracted particular attention as potential candidates for information storage devices.² In grid-like complexes, a set of metal ions are held in a regular array by organic ligands, which are displaced in perpendicular patterns. The metal ions are directing and sustaining the molecular architecture through their stereochemical coordination preferences, and from their interaction with the ligands result the redox,³ optical,^{3c,4} and magnetic properties.⁵

A first step in designing molecular devices based on grid-like complexes consists in the choice of suitable ligands in order to control the interactions between the metal ions and/or their electronic state. If the ligand offers an odd number of bridging atoms between the metal ions and constrains them in a planar arrangement, ferromagnetic couplings through a spin polarization mechanism can be demonstrated.⁶ For copper(II) [2 × 2] grid-like complexes with an even number of heteroaromatic bridging groups between the metallic centers, such as pyrazine⁷ or pyrazolate⁸ bridges, antiferromagnetic interactions between the metal centers were reported. Investigation by electron paramagnetic resonance on a dilute frozen solution of the magnetic behavior of copper(II) [2 × 2] grids with triazine- or pyrimidine-based ligands (an odd number of bridging atoms) showed ferromagnetic interactions for the triazine derivative and concentration-dependent competing magnetic interactions for the pyrimidine one.⁹ For the copper(II) grids, ferromagnetic interactions were reported especially in the case of single-atom linkages between the metal ions, Cu–O–Cu.¹⁰

Herein we report on the synthesis of two copper(II) [2 × 2] grid-like complexes with 2-phenylpyrimidine derivatives as ligands. Their crystal structures and magnetic properties have been investigated. We chose to use two ditopic bis(hydrazone) ligands functionalized with flexible relatively bulky substituents (Scheme 1) in order to prevent the intermolecular interactions between the metal ions and to minimize the distortions of the grid core induced by packing in the lattice.

Scheme 1. Structures of the Bis(hydrazone) Ligands L¹ and L² Used for Synthesis of the Copper(II) Grids



The reactions of copper(II) tetrafluoroborate with ligand L¹ and of copper(II) perchlorate with ligand L² [the two bis(hydrazone) ligands were obtained following reported procedures¹¹] afforded the [2 × 2] grid compounds [Cu₄(L¹)₄](BF₄)₈·10H₂O (**1**) and [Cu₄(L²)₄](ClO₄)₈ (**2**). The structural determinations by X-ray diffraction on a single crystal confirmed for both of them the grid formation (Figure 1). Compound **1** crystallizes in the chiral *P*2₁2₁2₁ orthorhombic space group [*a* = 18.537(3) Å, *b* = 28.794(4) Å, *c* = 31.529(5) Å, *V* = 16828(5) Å³], and **2** crystallizes in the centrosymmetric *C*2/*c* monoclinic space group [*a* = 28.760(2) Å, *b* = 16.635(2) Å, *c* = 31.940(3) Å, β = 105.286(8)°, *V* = 14740(3) Å³]. In these complexes, the copper(II) ions exhibit distorted octahedral geometries, with each metal ion being coordinated to six nitrogen atoms from two ligands positioned in an almost perpendicular fashion (each ligand contributes with one pyridine nitrogen, one pyrimidine nitrogen, and one hydrazone nitrogen). The Cu–N_{hydrazone} bond lengths are generally shorter than the Cu–N_{pyridine} and Cu–N_{pyrimidine} ones. The Cu–N_{hydrazone} bond lengths range from 1.943(7) to 2.091(7) Å in **1** and from 1.976(6) to 2.111(6) Å in **2**, while the Cu–N_{pyridine} and Cu–N_{pyrimidine} ones are between 2.065(6) and 2.324(6) Å in **1** and between 2.028(6) and 2.361(6) Å in **2** (Table S2 in the Supporting Information, SI). The Cu₄ units in compounds **1** and **2** present some rhombic distortions. The values of the Cu···Cu distances and Cu···Cu···Cu angles are presented in the schematic representations shown in Figure 1. The distortion of the Cu₄ unit from the planarity can be evaluated by measuring the distance between the centroids of the diagonals: 0.05 Å in compound **1**, where the four copper(II) ions are almost coplanar, and 0.265 Å in **2**. In both crystals, two from the eight anions, tetrafluoroborate in **1** and perchlorate in **2**,

Received: February 5, 2014

Published: April 22, 2014

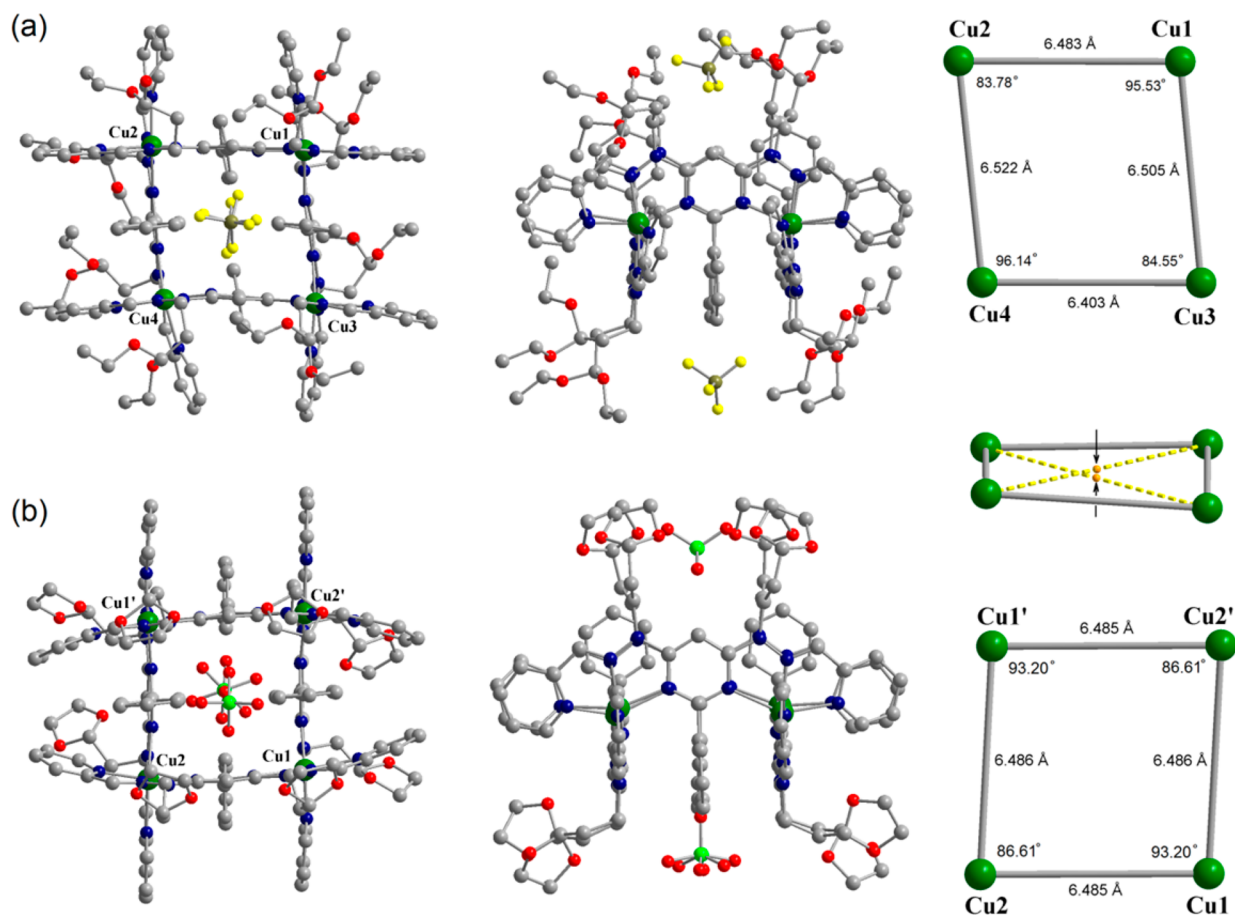


Figure 1. Orthogonal views of the cationic grid units in crystals **1** (a) and **2** (b). The hydrogen atoms and solvent molecules were omitted for clarity. From the tetrafluoroborate anions in **1** and the perchlorate anions in **2**, only those that are located in the proximity of the Cu₄ core were represented. One perchlorate anion in compound **2** is disordered on two crystallographic positions, with site occupancy factors of 0.5 each. Symmetry code: ' = 1 - x, y, 0.5 - z.

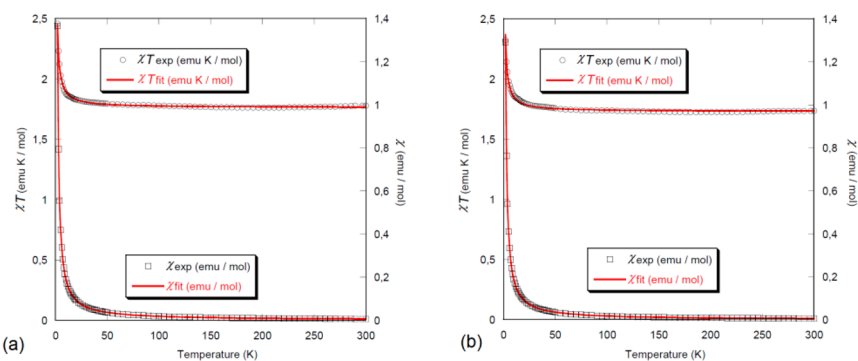


Figure 2. χT (open circles) and χ (open squares) as a function of the temperature plots for compounds **1** (a) and **2** (b). Full lines correspond to the fits.

are located in the proximity of the Cu₄ core, up and down, between the flexible axial substituents (Figure 1).

The magnetic properties of compounds **1** and **2** were investigated in the solid state in the 300–1.8 K temperature range with an applied field of 5 kOe. The two compounds present similar behavior (Figure 2). The χT values at room temperature (1.77 emu·K·mol⁻¹ for **1** and 1.74 emu·K·mol⁻¹ for **2**) correspond quite well to the expected value for four uncoupled copper(II) ions (1.65 emu·K·mol⁻¹ assuming $g = 2.1$). Upon cooling, the χT product remains almost constant down to ca. 50 K. Below 50 K, χT increases gradually up to 2.46 emu·K·mol⁻¹ at

1.8 K for **1** and 2.32 emu·K·mol⁻¹ at 1.8 K for **2**, indicating the occurrence of intramolecular ferromagnetic interactions.

Assuming a square spin topology, with a unique intramolecular magnetic interaction and molecules perfectly isolated, the data were fit using the following spin Hamiltonian, where all parameters have their usual meaning and the spin operator \mathbf{S} is defined as $\mathbf{S} = S_{\text{Cu1}} + S_{\text{Cu2}} + S_{\text{Cu3}} + S_{\text{Cu4}}$:

$$\mathbf{H} = -JS_{\text{Cu1}}S_{\text{Cu2}} - JS_{\text{Cu2}}S_{\text{Cu3}} - JS_{\text{Cu3}}S_{\text{Cu4}} - JS_{\text{Cu4}}S_{\text{Cu1}} + g\beta HS$$

The fits lead the following values: $J = +1.04 \text{ cm}^{-1}$ and $g = 2.17$ for **1** and $J = +0.97 \text{ cm}^{-1}$ and $g = 2.15$ for **2**.

In both compounds, the copper(II) ions exhibit distorted octahedral geometries with Cu–N bond lengths in the wide range from 1.943(7) to 2.361(6) Å with a quite irregular distribution for the four copper(II) ions in the grid **1** (Figure 3

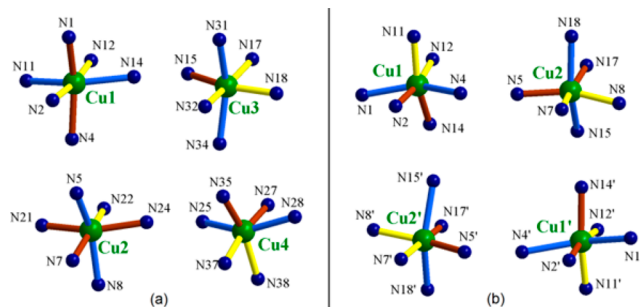


Figure 3. Perspective views of the metal-ion coordination spheres in the grid complexes **1** (a) and **2** (b). The Cu–N bonds with lengths in the range of 1.94–2.08 Å are labeled with yellow, those in the range of 2.08–2.20 Å with brown, and those over 2.20 Å with blue. Symmetry code: $' = 1 - x, y, 0.5 - z$.

and Table S2 in the SI). Taking into account only the longer Cu–N bonds (over 2.20 Å) and assuming the coordination spheres of copper(II) ions as elongated octahedra, the orthogonality of the magnetic orbitals can be proposed as a coupling mechanism more likely than spin polarization (due to the alternate arrangement of the long axes around the squares).

In conclusion, the magnetic behavior of the two copper(II) [2 × 2] grid-like complexes showed that the pyrimidine bridges are able to mediate ferromagnetic interactions. Modulation of the magnetic interactions between the metal ions through external stimuli (e.g., insertion of a smaller anion, halide, in the grid cavity) represents a target in manipulation of these nanoobjects for future applications.

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data in CIF format, synthesis and characterization data (elemental chemical analyses and IR spectra), a summary of the crystallographic data and the structure refinement, and selected bond lengths in compounds **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

A.M.M. acknowledges financial support of a Marie Curie Intra-European Fellowship (Project 023627).

DEDICATION

Dedicated to Professor Marius Andruh on the occasion of his 60th birthday.

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