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Spin Control in Oxamato-Based Manganese(II)–Copper(II) Coordination Polymers with Brick-Wall Layer Architectures

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Supporting Information

ABSTRACT: Two new heterobimetallic manganese(II)–copper(II) coordination polymers of formulas $[\text{Mn}_2\text{Cu}_2(\text{Me}_3\text{mpba})_2(\text{H}_2\text{O})_6] \cdot 8\text{H}_2\text{O}$ (**1**) and $[\text{Mn}_2\text{Cu}_2(\text{Me}_4\text{ppba})_2(\text{H}_2\text{O})_6] \cdot 8\text{H}_2\text{O}$ (**2**) [Me_3mpba = 2,4,6-trimethyl-*N,N'*-1,3-phenylenebis(oxamate) and Me_4ppba = 2,3,5,6-tetramethyl-*N,N'*-1,4-phenylenebis(oxamate)] have been synthesized following a molecular-programmed self-assembly method from the corresponding dicopper(II) complexes acting as metalloligands toward Mn^{II} ions. **1** and **2** consist of neutral $\text{Mn}^{\text{II}}_2\text{Cu}^{\text{II}}_2$ layers with a brick-wall structure made up of oxamato-bridged $\text{Mn}^{\text{II}}\text{Cu}^{\text{II}}$ chains connected through double meta- (**1**) and para-substituted (**2**) permethylated phenylene spacers. Overall magnetic (**1**) and nonmagnetic (**2**) layer ground states result from the ferro- and antiferromagnetic interchain interactions between the oxamato-bridged $\text{Mn}^{\text{II}}\text{Cu}^{\text{II}}$ ferrimagnetic chains across *m*- and *p*-phenylene spacers, respectively. Interestingly, compound **1** exhibits a long-range ferromagnetic ordering with a rather high Curie temperature (T_C) of 20.0 K.

Ligand design plays a crucial role in the search for new examples of multidimensional coordination polymers showing interesting and predictable structures and magnetic properties,^{1–4} referred to as metal–organic polymers (MOPs). First, it allows one to gain control of the final dimensionality and topology of the MOP, and, second, it provides a way to efficiently transmit the magnetic interactions between the metal ions in a controlled manner. In this respect, the use of the so-called “complex-as-ligand” strategy, where a preformed precursor complex acts as a ligand (metalloligand) toward free paramagnetic metal ions, shows clear advantages against the more spread serendipitous self-assembly methods for the obtention of open-framework magnets, that is to say, molecular-based compounds combining both an open-framework two- (2D) or three-dimensional (3D) porous structure and spontaneous magnetization below a critical temperature (T_C).⁵

During the last years, our research group has succeeded in developing a new class of oxamato-based MOPs by means of molecular-programmed self-assembly methods based on ligand design.⁶ Along this line, our strategy consisted of using oxamato-based metallacyclic precursor complexes with predetermined

magnetic properties via the spin-polarization mechanism.⁷ For instance, two double-stranded dicopper(II) metallacyclopentane precursor complexes, $[\text{Cu}_2(\text{mpba})_2]^{4-}$ and $[\text{Cu}_2(\text{ppba})_2]^{4-}$ [mpba = *N,N'*-1,3-phenylenebis(oxamate) and ppba = *N,N'*-1,4-phenylenebis(oxamate)] were successfully employed as effective ferro- and antiferromagnetic synthons, respectively, in the construction of a family of hexacopper(II) complexes with predictable magnetic properties.⁸ This strategy was subsequently extended to higher-dimensionality MOPs.⁶ Thus, $[\text{Cu}_2(\text{mpba})_2]^{4-}$ acting as a tetrakis(bidentate) metalloligand toward bis(chelated) Co^{II} ions yielded a 2D MOP of formula $[\text{Co}_2\text{Cu}_2(\text{mpba})_2(\text{H}_2\text{O})_6] \cdot 6\text{H}_2\text{O}$ with a “brick-wall” structure of (6,3) net topology and metamagnetic behavior.^{6a}

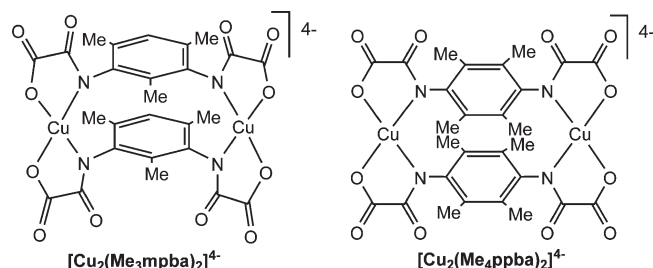
In this Communication, we show that 2D MOPs with such a brick-wall rectangular structure can be obtained when using the related permethylated dicopper(II) analogues $[\text{Cu}_2(\text{Me}_3\text{mpba})_2]^{4-}$ and $[\text{Cu}_2(\text{Me}_4\text{ppba})_2]^{4-}$ [Me_3mpba = 2,4,6-trimethyl-*N,N'*-1,3-phenylenebis(oxamate) and Me_4ppba = 2,3,5,6-tetramethyl-*N,N'*-1,4-phenylenebis(oxamate)] (Chart 1) as tetrakis(bidentate) metalloligands toward bis(chelated) Mn^{II} ions (Scheme 1). Herein we report the synthesis and structural and magnetic characterization of two new manganese(II)–copper(II) 2D MOPs of formulas $[\text{Mn}_2\text{Cu}_2(\text{Me}_3\text{mpba})_2(\text{H}_2\text{O})_6] \cdot 8\text{H}_2\text{O}$ (**1**) and $[\text{Mn}_2\text{Cu}_2(\text{Me}_4\text{ppba})_2(\text{H}_2\text{O})_6] \cdot 8\text{H}_2\text{O}$ (**2**). Compounds **1** and **2** constitute a rare example of control of the spin coupling in MOPs by the topology of the bridging ligand.

Compounds **1** and **2** were both obtained as a pale-green polycrystalline powder and deep-green cubic crystals, respectively, by slow diffusion in an H-shaped tube of aqueous solutions of $\text{Li}_4[\text{Cu}_2\text{L}_2] \cdot n\text{H}_2\text{O}$ [L = Me_3mpba ($n = 8$) and Me_4ppba ($n = 7$)] and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (1:2 molar ratio) at room temperature. The crystal structure of **2** has been solved by single-crystal X-ray diffraction using synchrotron radiation at the BM16 beamline in the ESRF. Our attempts to obtain X-ray quality crystals of **1** were unsuccessful. However, its powder X-ray diffraction pattern was similar to the theoretical one found for the analogue $[\text{Co}_2\text{Cu}_2(\text{mpba})_2(\text{H}_2\text{O})_6] \cdot 6\text{H}_2\text{O}$,^{6a} suggesting thus a common “brick-wall” layer structure (Figure S1 in the Supporting Information).

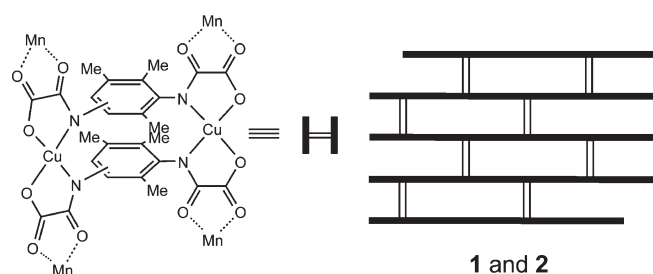
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Chart 1



Scheme 1. Postulated Brick-Wall Rectangular Layer Architecture of the 2D MOPs Resulting from the Self-assembly of Dicopper(II) Metallacyclophane Anionic Complexes and Bis(chelated) Mn^{II} ions



Compound **2** crystallizes in the centrosymmetric $P2_1/n$ space group. The structure of **2** consists of neutral manganese(II)–copper(II) 2D networks, $[\text{Mn}_2\text{Cu}_2(\text{Me}_4\text{ppba})_2(\text{H}_2\text{O})_6]$ (Figures 1 and S2 in the Supporting Information), and free crystallization water molecules. Each dicopper(II) metallacyclophane entity acts as a tetrakis(bidentate) ligand through the carbonyl oxygen atoms of the oxamate ligand atoms toward *cis*-diaquamanganese(II) units, yielding a corrugated brick-wall rectangular layer with a (6,3) net topology growing in the *bc* plane (Figure 1). There are six copper atoms within each rectangular cell unit of **2**, which occupy the four corners and the middle point of the two long edges of the rectangle, whereas four Mn^{II} ions sit at the one-fourth and three-fourth points of each long edge (Figure 1a). Each $\text{Mn}^{\text{II}}_2\text{Cu}_2$ layer of **2** is made up of an extended array of oxamato-bridged zigzag $\text{Mn}^{\text{II}}\text{Cu}^{\text{II}}$ chains running parallel to the crystallographic *c* axis, which are connected through double para-substituted tetramethylated phenylene spacers (Figure 1b). The shortest intralayer $\text{Cu}\cdots\text{Cu}$ and $\text{Cu}\cdots\text{Mn}$ distances are 7.9606(5) and 5.4105(4)–5.4211(4) Å, respectively.

The Cu(1) atom has a five-coordinated square pyramid (CuN_2O_3), with two amidate nitrogen atoms [$\text{Cu}-\text{N} = 1.9681(14)$ – $1.9869(14)$ Å] and two carboxylate oxygen atoms [$\text{Cu}-\text{O} = 1.9832(12)$ – $1.9833(12)$ Å] from the oxamato groups of the Me_4ppba ligands building the basal plane, with the apical position being occupied by a weakly coordinated water molecule [$\text{Cu}-\text{Ow} = 2.4754(15)$ Å]. On the other hand, the Mn(1) atom is six-coordinated (MnO_6), with two *cis*-coordinated water molecules [$\text{Mn}-\text{Ow} = 2.1439(13)$ – $2.2297(13)$ Å] and four carbonyl oxygen atoms [$\text{Mn}-\text{O} = 2.1415(12)$ – $2.2108(12)$ Å] from two oxamato groups of the Me_4ppba ligands forming distorted octahedral surroundings.

In the crystal lattice of **2**, the adjacent corrugated $\text{Mn}^{\text{II}}_2\text{Cu}_2$ layers stack above each other in an eclipsed manner to give an infinite array of interdigitated layers along the $[101]$ direction

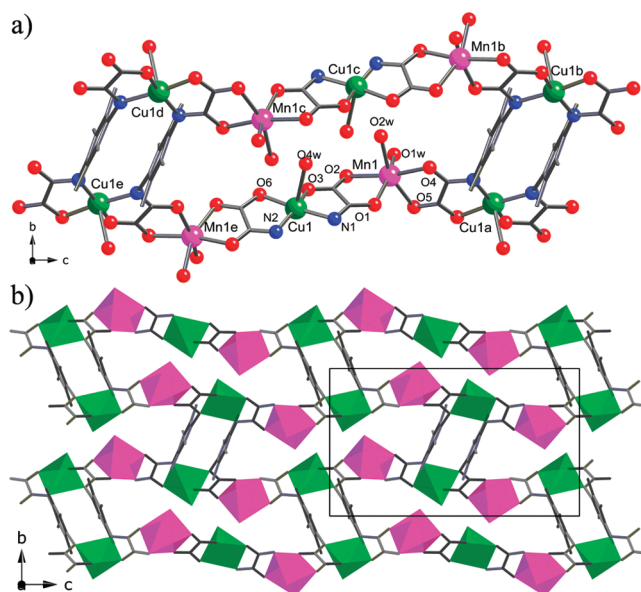


Figure 1. (a) Perspective view of the unit cell of **2** with the atom labeling of the metal environments (hydrogen atoms are omitted for clarity) [symmetry codes: (a) $x + 1/2, -y + 1/2, z + 1/2$; (b) $-x + 1/2, y + 1/2, -z + 1/2$; (c) $-x, -y + 1, -z$; (d) $-x - 1/2, y + 1/2, -z - 1/2$; (e) $x - 1/2, -y + 1/2, z - 1/2$]. (b) Projection view of the 2D neutral network of **2** along the *a* axis.

(Figure S2a in the Supporting Information). This zipper-type eclipsed packing of neighboring layers leads to small nanopores along the *c* axis, which are occupied by hydrogen-bonded crystallization water molecules (Figure S2b in the Supporting Information). The shortest interlayer $\text{Cu}\cdots\text{Cu}$, $\text{Cu}\cdots\text{Mn}$, and $\text{Mn}\cdots\text{Mn}$ distances are 7.9616(5), 5.1333(4), and 6.9182(5) Å, respectively.

The direct-current magnetic properties of **1** and **2** in the form of $\chi_{\text{M}}T$ versus *T* plots (with χ_{M} being the molar magnetic susceptibility per Cu_2Mn_2 unit) are completely different (Figure 2). At room temperature, the values of $\chi_{\text{M}}T$ for **1** and **2** (8.13 and 7.46 $\text{cm}^3 \text{mol}^{-1} \text{K}$, respectively) are lower than those expected for the sum of two Cu^{II} and two Mn^{II} noninteracting ions ($\chi_{\text{M}}T = 9.54 \text{ cm}^3 \text{mol}^{-1} \text{K}$ with $g_{\text{Mn}} = 2.0$, $g_{\text{Cu}} = 2.1$, $S_{\text{Mn}} = 5/2$, and $S_{\text{Cu}} = 1/2$), indicating that a strong antiferromagnetic coupling between Cu^{II} and Mn^{II} ions through the oxamate is operative at room temperature. Upon cooling, $\chi_{\text{M}}T$ for **1** decreases and attains a minimum around 60 K (Figure 2), and then $\chi_{\text{M}}T$ rapidly increases to reach a maximum value of 186 $\text{cm}^3 \text{mol}^{-1} \text{K}$ at about 15.0 K, due to saturation effects. The presence of a $\chi_{\text{M}}T$ minimum for **1** is characteristic of an overall ferrimagnetic behavior resulting from the moderately strong antiferromagnetic interaction between the Mn^{II} and Cu^{II} ions through the oxamato bridge. In this case, it would mask the moderately weak ferromagnetic interaction between the Cu^{II} ions across the double *m*-phenylene spacers via the spin-polarization mechanism,^{7a} as was previously observed in the analogue $[\text{Co}_2\text{Cu}_2(\text{mpba})_2(\text{H}_2\text{O})_6] \cdot 6\text{H}_2\text{O}$. On the contrary, $\chi_{\text{M}}T$ for **2** continuously decreases upon cooling, and it almost vanishes at 2.0 K, reaching a value of $\chi_{\text{M}}T$ of 0.08 $\text{cm}^3 \text{mol}^{-1} \text{K}$ (Figure 2). This overall antiferromagnetic behavior results from the very strong antiferromagnetic interaction between the Cu^{II} ions across the double *p*-phenylene spacers through the spin-polarization mechanism.^{7b} In this case, it would dominate over

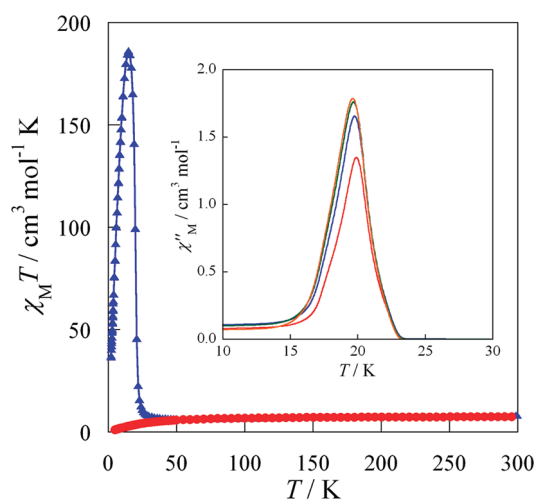


Figure 2. Temperature dependence of $\chi_M T$ for **1** (\blacktriangle) and **2** (\bullet) under an applied magnetic field of 1 T ($T \geq 50$ K) and 100 G ($T < 50$ K). The inset shows the temperature dependence of χ_M'' for **1** with a ± 1.0 G field oscillating at different frequencies (10–1400 Hz). The solid lines are eye guides.

the moderately strong antiferromagnetic interaction between the Mn^{II} and Cu^{II} ions through the oxamate bridge, thus leading to a nonmagnetic ground state for each $\text{Mn}^{\text{II}}_2\text{Cu}^{\text{II}}_2$ layer of **2**. The lack of a maximum of χ_M precludes the occurrence of an antiferromagnetic 3D ordering in the temperature range investigated (2–300 K).

Interestingly, compound **1** undergoes an abrupt paramagnetic-to-ferromagnetic phase transition as revealed by the temperature dependence of the field-cooled magnetization (FCM; Figure S3 in the Supporting Information). The FCM curve, measured by cooling the sample within a small field of 100 G, exhibits an abrupt increase below 25.0 K, thereby suggesting the onset of a 3D ferromagnetic transition resulting from the ferromagnetic interactions between the $\text{Mn}^{\text{II}}_2\text{Cu}^{\text{II}}_2$ layers of **1**. Indeed, the long-range magnetic ordering is confirmed by the alternating-current magnetic properties in the form of the χ_M'' versus T plots (with χ_M'' being the out-of-phase molar magnetic susceptibility per Cu_2Mn_2 unit) at different frequencies (ν) of the ± 1 G oscillating field. Hence, χ_M'' becomes nonzero below 25.0 K, and nonfrequency-dependent maxima are observed at $T_C = 20.0$ K (inset of Figure 2). Indeed, the ferromagnetic nature of the transition is confirmed by the magnetic hysteresis loop at 2.0 K (inset of Figure S3b in the Supporting Information), which is characteristic of a soft magnet, as evidenced by the moderately low value of the coercive field ($H_c = 100$ G).

In conclusion, dicopper(II) metallacyclophanes with permethylated *m*- and *p*-phenylenebis(oxamate) bridging ligands have been used as effective ferro- and antiferromagnetic units, respectively, for the obtention of two novel manganese(II)–copper(II) 2D MOPs with a brick-wall layer structure. The dramatically different magnetic behavior of the resulting 2D MOPs depending on the meta- and para-substitution pattern of the bridging ligand represents thus a successful extension of the concept of ferro- or antiferromagnetic coupling units for control of the spin coupling in coordination polymers on the way toward the rational design of open-framework magnets.

■ ASSOCIATED CONTENT

S Supporting Information. Experimental preparation, analytical and spectroscopic characterization of ligands, dicopper(II) complexes and **1** and **2** X-ray crystallographic data, additional figures (S1–S3), and a crystallographic information file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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