Self-assembly of square-lattice copper sheets displaying intra-ferromagnetism

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A homoleptic copper(II) complex supported by methylimidodiacetate \([\text{CH}_3\text{N(CH}_2\text{COO)}_2^{2–} = \text{MIDA}]\) has been prepared and characterized by elemental, infra-red, X-ray diffraction and magnetic methods. The complex assembles as a two-dimensional lattice in which the copper centers are arranged in a square grid, bridged by the carboxylate moieties of the ligand. \([\text{CuII}_2\text{MIDA}_4]_{14}\) crystallizes in the tetragonal system \(P-4_2_1_2\); \(c = 9.8943(5), b = 9.8943(5), c = 14.4687(7)\,\text{Å}, Z = 8, R = 0.0495\). Each CuII atom displays severely distorted square pyramidal geometry \((\gamma = 0.44)\) and is bridged to four additional copper centers by a \(\text{syn-anti}\) arrangement of the carboxylate groups. Within the sheet, the copper centers are separated by approximately 4.96 Å. The sheets are layered by arranging the copper squares directly on top of one another, resulting in parallel channels that extend throughout the material. Variable temperature magnetic susceptibility measurements reveal the presence of ferromagnetic exchange between the spin carriers within each two-dimensional sheet and antiferromagnetic exchange across the layers.

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1. Introduction

The self-assembly of supramolecular structures has received considerable attention in recent years, especially in the area of transition metal coordination polymers [1–9]. The fascinating topologies of these advanced materials have led to potential applications in inclusion phenomena, gas storage/separation [10–14], catalysis [15,16], guest exchange [17,18], and molecular-based magnets [19–22]. Consequently, research is focused on the assembly of metal ions bearing a variety of multifunctional organic ligands in order to ascertain desirable characteristics and hopefully develop synthetic routes toward their rational design. Infinite two-dimensional layer-type structures containing transition metals have also been pursued as materials with potentially long range order but low-dimensionality [23–29].

In addition to their prominent role as bridging ligands in the active sites of numerous metalloenzymes [30–34], multi-carboxylates of various flexibilities and sizes have been shown to employ a variety of bonding configurations, including \(\text{syn-syn, syn-anti, and anti-anti}\), resulting in the isolation of a plethora of intriguing multi-dimensional structures [35–42]. Of interest to the present paper, carboxylate-based ligands have been used to assemble multi-nuclear copper structures, either homoleptically or in combination with \(N\)-heterocyclic ligands, with varying magnetic interactions based on the bridging conformation and metal geometry [35–49]. Arrangements in which the copper centers form \(2 \times 2\) grids, whether as square or rhombohedral tetranuclear copper complexes [50–61], or as the analogous two-dimensional extended networks, are few [29,62–71].

Herein, we report the synthesis, characterization and magnetism of a two-dimensional homoleptic copper sheet in which the metal centers are arranged in a perfect square grid and display ferromagnetic exchange within the sheet. While ferromagnetically-coupled CuII tetramers are rare [54–61]; to the best of our knowledge the complex reported herein represents the first infinite sheet comprised of ferromagnetically coupled CuII square grids.

2. Experimental

2.1. Synthesis of the complexes

Compound 1 was prepared by the deprotonation of \(N\)-methylimidodiacetic acid \((\text{H}_3\text{MIDA}, \text{Acros Organics}, 5.00\,\text{g}, 34.0\,\text{mmol})\) by two equivalents of NaOCH\(_3\) (Aldrich, 25% wt. in MeOH, 18.6 mL, 68.0 mmol) in methanol. The suspension was allowed to stir overnight at room temperature. The white solid was filtered and dried under vacuum at 115 °C \((\text{Na}_2\text{MIDA}, 5.99\,\text{g}, 31.3\,\text{mmol}, 92.2\%\) yield).

\(^1\text{H NMR (20 °C, 300 MHz, D}_2\text{O):} \delta = 2.94 \,(\text{s, 4H, CH}_2), 2.11 \,(\text{s, 3H, CH}_3), \,\text{31C NMR (20 °C, 75 MHz, D}_2\text{O):} \delta = 178.9 \,(\text{COO}^-), 61.0 \,(\text{CH}_2), 41.8 \,(\text{CH}_3), \,\text{IR (Nujol, cm}^{-1}\text{):} \nu = 3383 \,(\text{w, 2849 (s, 1318 (w, 1229 (w, 1186 (m, 1139 (w, 1125 (s, 1076 (s, 1048 (s, 1005 (s, 993 (s, 966 (s, 913 (s, 892 (w, 767 (m, 752 (w, 696 (w, 624 (m, 592 (w.}

Compound 2 was prepared by the addition of \(\text{Na}_2\text{MIDA} 1\) \((0.5050\,\text{g}, 2.64\,\text{mmol})\) to \(\text{CuCl}_2\cdot2\text{H}_2\text{O}\) (Fisher Scientific Company, 0020-1693/$ - see front matter © 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.ica.2011.01.032
0.4545 g, 2.53 mmol). The resulting royal blue solution was heated at 80 °C and allowed to stir overnight. The solution was concentrated by solvent evaporation and royal-blue, rectangular plate crystals were obtained from a 10:1 ethanol:water mixture upon standing at 4 °C (0.2606 g, 1.25 mmol, 47.3% yield). Anal. Calc. for C_{176}H_{76}CuNO_{2}: C, 28.78; H, 3.38; N, 6.71. Found: C, 28.54; H, 3.42; N, 6.54%. IR (Nujol mull, cm^{-1}): ν 3368 (w), 2923 (m), 2854 (m), 2363 (m), 2326 (w), 1653 (w), 1576 (m), 1457 (m), 1419 (m), 1379 (w), 1337 (m), 1316 (s), 1288 (m), 1257 (s), 1184 (s), 1154 (s), 1105 (m), 1043 (s), 1010 (s), 922 (s), 884 (s), 752 (s), 630 (m), 569 (w).

2.2. Single crystal X-ray diffraction studies

The results presented for compound 2 are the best of several trials. Crystals of 2 were mounted on a thin glass fiber using paraffin oil. Data were collected on a Bruker-AXS SMART 1k CCD diffractometer and collected with a sequence of 0.3° scans at 0, 120, and 240° in ϕ. Initial unit cell parameters were determined from 60 data frames collected at the different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied [72]. Systematic absences in the diffraction data set and unit-cell parameters were consistent with tetragonal P-4 21 c. The structure was solved by direct methods, completed with difference Fourier synthesis, and refined with full-matrix least-squares procedures based on F^2. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All scattering factors are contained in several versions of the SHELXTL program library, version 6.12 [73]. Crystallographic data are reported in Table 1.

2.3. Physical measurements

NMR spectra were recorded at 20 °C with a 300 MHz Mercury Plus Varian Instrument with Oxford magnet. Elemental analysis was performed on an EAS 1108 apparatus from Fisons Instruments SPA. The IR spectra were recorded in Nujol mulls with a Perkin-Elmer FT-IR System Spectrum GX spectrometer (4000–400 cm⁻¹). Variable-temperature dc magnetic susceptibility data were collected using a Quantum Design MPMS-XL7 SQUID magnetometer. The measurements were performed on polycrystalline samples wrapped in a polyethylene membrane under a field ranging from 0 to 7 T between 1.8 and 300 K. Experimental data were corrected for the sample holder and for diamagnetic contributions calculated from Pascal constants [74].

3. Results and discussion

Reaction of one equivalent of the dianionic ligand 1, MIDA^2−, with hydrated CuCl2 resulted in the formation of compound 2 as royal blue crystals. The molecular structure was determined by single crystal X-ray diffraction and can be represented as [CuII^4(MIDA)_{4}]. The compound crystallizes in the tetragonal space group P-4 21 c and consists of a polymeric 2D network. The CuII metal centers are bridged exclusively by the carboxylate moieties of the ligand and the geometry about each symmetry-generated Cu^{II} ion may be considered as severely distorted square pyramidal (τ = 0.44) [75] (Fig. 1). The nitrogen and two oxygen atoms of the tridentate ligand surround the metal center in a mer fashion, occupying three of the basal sites [Cu1–N1 = 2.001(3) Å, Cu1–O1 = 1.963(3) Å, Cu1–O1 = 1.966(4) Å, O1–Cu1–O1 = 166.06(12)°]. The geometric constraints imposed by the chelating ligand ensure bonding of the oxygen atoms in an anti configuration. Alternatively, two carboxylate oxygen atoms from two additional ligands occupy the final basal site [Cu1–O2A = 2.039(4) Å] and the apical site [Cu1–O4A = 2.132(4) Å], bridging the copper center to two additional copper ions in syn fashion. As such, each carboxylate group bridges two metal centers in a syn--anti configuration. The CuII ions are arranged in a 2D square grid with a distance of 4.96 Å between the metal centers forming cubic channels. The packing along the a-axis shows an A–B–A type arrangement of the layers with a distance of 7.23 Å between the closest copper centers of different layers (Fig. 2). Planarity, non-penetration, and separation of layers are imposed by the geometric features of the structure. Examining the structure along the b-axis highlights the alternating position of the ligands above and below the plane of the metal centers, minimizing the steric hindrance.

Besides the one example of a homoleptic MIDA cuprate complex, Na₂[Cu(MIDA)₂] [76], the majority of Cu-MIDA complexes reported to date contain additional N-heterocyclic ligands and form linear chains via carboxylate bridging [44,45]. Copper complexes of the analogous iminodiacetate ligand, IDA, also engage in the

### Table 1

| Crystal data and structure analysis results for 2. |
| --- | --- |
| Formula | C_{176}H_{76}CuNO_{2} |
| M_w | 208.66 |
| Crystal system | tetragonal |
| Space group | P-4 21 c |
| a (Å) | 9.8943(5) |
| b (Å) | 9.8943(5) |
| c (Å) | 14.4687(7) |
| α (°) | 90 |
| β (°) | 90 |
| γ (°) | 90 |
| V (Å^3) | 1416.44(12) |
| Z | 8 |
| Radiation (Kα, Å) | 0.71073 |
| T(K) | 296(2) |
| D_cal (g cm⁻³) | 1.957 |
| μ_max (mm⁻¹) | 3.04 |
| F(000) | 840 |
| R, wR² | 0.0495, 0.1294 |
| GoF | 1.073 |

4. R = Σ||F_o|| - |F_i|/Σ||F_i||, wR² = Σ||F_o|| - |F_i|^2/2Σw_i||F_i||^2/2.
The data are plotted as magnetic field of 1000 Oe over the temperature range 1.8–300 K. were performed on the crushed crystalline sample in an applied when the bridge binds both equatorial and axial sites.\(^4\)\(^9\). oxygen atoms are bound in equatorial sites, or antiferromagnetic of the interaction depending on the site of ligation of the carboxyl-
sion of magnetic information between the copper ions, the nature
of interaction between the CuII ions in the 2D sheet. Below 7 K, we observe a sharp decrease in the
value to 0.72 cm\(^3\) K mol\(^{-1}\) at 7 K, indicative of ferromag-
tic coupling between the CuII ions in the 2D sheet. 7 K, we observe a sharp decrease in the
value to 0.72 cm\(^3\) K mol\(^{-1}\) at 1.8 K, suggesting antiferromagnetic coupling between the
[Cu\(^{II}\)\(\text{MIDA}_4\)]\(_n\) layers.

Based on a repeating tetranuclear divalent copper unit, the magnetic data were analyzed with the following Heisenberg Hamiltonian:

\[ H = -2J(S_1 S_2 + S_3 S_4) \]

where \(J\) is the intramolecular exchange interaction between Cu\(^{II}\) ions in the tetramer and \(S\) is the spin operator for each \(S = 1/2\) Cu\(^{II}\) center.

The expression of the magnetic susceptibility is:

\[ 
\chi_M T = \frac{\mu^2 N g^2}{3k} \left\{ \frac{6(5 \exp(2x) + \exp(-2x) + 2)}{5 \exp(2x) + 3 \exp(-2x) + \exp(-4x) + 7} \right\} 
\]

where \(x = J/kT\). A least squares fit leads to the following parameters: \(J = 1.3 \text{ cm}^{-1}\) and \(g = 2.2\).

These results are in contrast to other reported examples of Cu-
MIDA or IDA chains, which display antiferromagnetic coupling across the carboxylate bridges [43–49,77–81]. However, weak fer-
romagnetic interactions have been reported in the hydrogen-bond-
assembled linear chains of Cu-IDA-HB2zm units [46], likely due to the orthogonality of the magnetic orbitals on adjacent monomers. In addition, ferromagnetic exchange has also been observed in se-
tected tetranuclear Cu complexes [54–61,77]. The obtained coupling constant (\(J = 1.3 \text{ cm}^{-1}\)) is smaller than would be expected for an extended Cu sheet. In the complex, each copper ion is bridged to four additional copper ions via syn–anti carboxylate bridges. Preferably, ferromagnetic exchange is fa-
voured when the bridging ligands coordinate in equatorial positions
on the metal center [49]. However, the geometry of the metal center suffers from severe distortion, lying somewhere between square pyramidal and trigonal bipyramidal. As such, the metal
atoms are not arranged ideally to support stronger ferromagnetic interactions.

In summary, complexation of MIDA to Cu\(^{II}\) ions results in the self-assembly of extended two-dimensional sheets in which the Cu centers are arranged in a perfect square lattice. Ferromagnetic interactions dominate intra-molecularly, with antiferromagnetic interactions occurring intermolecularly between the layers. The significance is such that complex 2 represents the first example of extended two-dimensional ferromagnetism within a square lat-
tice Cu sheet. Interestingly, previous studies involving the coordi-
nation of MIDA to transition metal centers, including Cu, have not resulted in the formation of networks like those described herein and studies are currently underway to establish the factors governing self-assembly in this case.

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Appendix A. Supplementary material

CCDC 789919 contains 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.

Supplementary data associated with this article can be found, in

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