CRYSTAL GROWTH & DESIGN

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Topologically Unique 2D Heterometallic Cu^{II}/Mg Coordination Polymer: Synthesis, Structural Features, and Catalytic Use in Alkane Hydrocarboxylation

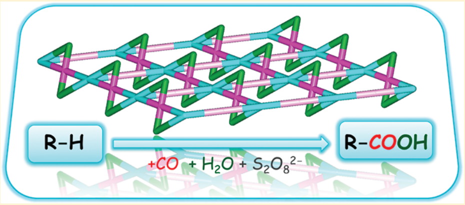
Alexander M. Kirillov,*,[†] Yauhen Y. Karabach,[†] Marina V. Kirillova,[†] Matti Haukka,[‡] and Armando J. L. Pombeiro*,[†]

[†]Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Technical University of Lisbon, Av. Rovisco Pais, 1049-001 Lisbon, Portugal

[‡]Department of Chemistry, University of Eastern Finland, P.O. Box 111, FIN-80101 Joensuu, Finland

S *Supporting Information*

ABSTRACT: The new two-dimensional (2D) heterometallic Cu^{II}/Mg coordination polymer $[Cu_2Mg_2(\mu\text{-Htea})_2(\mu_6\text{-pma})(H_2O)_6]_n \cdot 6nH_2O$ (**1**) with an unprecedented $[Cu_2Mg(\mu\text{-O})_2(\mu\text{-COO})_2]^-$ core has been easily generated by aqueous medium self-assembly from copper(II) nitrate, triethanolamine (H_3tea), magnesium hydroxide, and pyromellitic acid (H_4pma). The crystal structure of **1** is composed of infinite interdigitated 2D metal−organic layers that extend via H-bonds into an intricate 3D supramolecular framework. The topological analysis of **1** discloses a binodal 2,4-connected underlying 2D net with the unique topology described by the point symbol of $(6^4 \cdot 8 \cdot 10)(6)$, further simplification of which leads to an uninodal 4-connected net with the **sql** topology. Apart from representing a very rare example of the heterometallic Cu/Mg coordination network, compound **1** also acts as an efficient catalyst precursor for the mild single-pot hydrocarboxylation of linear and cyclic C_n (n = 5−9) alkanes into the corresponding C_{n+1} carboxylic acids.



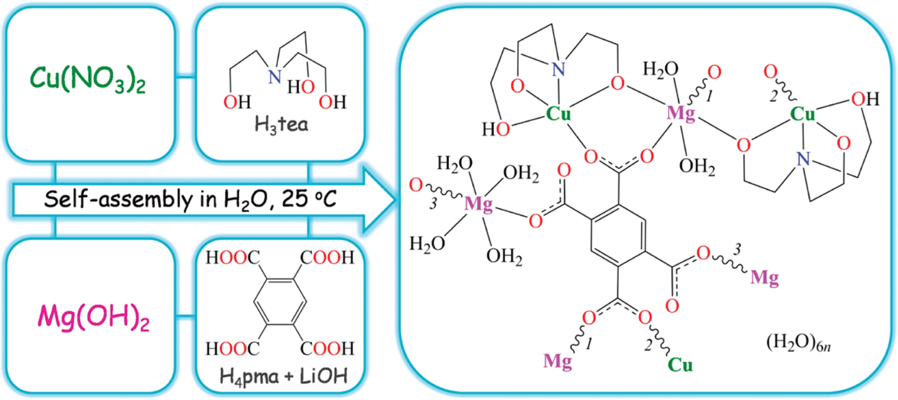
The research on coordination polymers or metal−organic frameworks has recently attracted a great deal of attention within the fields of crystal engineering and inorganic, coordination, and materials chemistry, particularly in view of the structural diversity and promising applications of such compounds as multifunctional materials.[1−3] In contrast to the very broad use of transition metals as nodes in the construction of coordination networks, the application of the common s-block metal centers (i.e., Na, K, Mg, Ca) for such a purpose has been explored to a lesser extent,[3] in spite of their versatile coordination and supramolecular behaviors, nontoxic nature, and widespread presence in diverse natural environments and living systems. Moreover, heterometallic coordination polymers incorporating both a transition and an alkali or alkaline earth metals are even less common,[1−4] although the introduction of two different metal centers can alter the structural, topological, and physicochemical characteristics of the resulting network material.

Within our general projects on the design of new metal−organic networks,[5] we have recently reported a number of heterodimetallic Cu^{II}/M (M = Na, K) coordination polymers, which also showed some notable structural, host−guest, magnetic, and catalytic features.[6,7] In particular, series of metal−organic networks have been generated by a versatile aqueous medium self-assembly protocol, using various Cu-aminopolyalcoholate building blocks, aromatic polycarboxylate spacers, and the corresponding alkali metal hydroxides that acted simultaneously as pH-regulators and extra nodes or linkers.[6] In pursuit of these studies, the first objective of the present work consisted in further extending the synthetic strategy and the type of the heterometallic coordination network thereof, namely by introducing magnesium as an alkaline earth metal ion. In this regard, it should be highlighted that heterometallic Cu/Mg coordination polymers are extremely rare,[8] as attested by the search of the Cambridge Structural Database (CSD).[4] Furthermore, since the application of Cu containing coordination polymers in oxidation catalysis also remains an underexplored area of research,[9] the second objective of this study was to probe the catalytic function of the newly obtained Cu/Mg product.

Hence, we report herein the facile self-assembly synthesis, X-ray crystal structure, detailed topological analysis, and catalytic application of the new 2D heterometallic Cu^{II}/Mg coordination polymer $[Cu_2Mg_2(\mu\text{-Htea})_2(\mu_6\text{-pma})(H_2O)_6]_n \cdot 6nH_2O$ (**1**), which features an unprecedented $[Cu_2Mg(\mu\text{-O})_2(\mu\text{-COO})_2]^-$ core and a unique net topology, as well as acts as an efficient and versatile catalyst precursor for the mild hydrocarboxylation of alkanes under homogeneous conditions. The combination in water, at room temperature (rt, ∼25 °C), and in air, of $Cu(NO_3)_2$ and triethanolamine (H_3tea) as a main ligand source, followed by the alkalization of the obtained mixture with $Mg(OH)_2$ (pH regulator and building block) and the addition of lithium pyromellitate (spacer source) generated

Received: November 6, 2011
Revised: January 22, 2012
Published: January 27, 2012

Scheme 1. Aqueous Medium Self-assembly Synthesis and Structural Formula of 1[a]



[a]Numbers *1*, *2*, and *3* correspond to extensions of polymeric motifs.

in situ from LiOH and pyromellitic acid (H_4pma, 1,2,4,5-benzenetetracarboxylic acid) results in the self-assembly formation of **1** (Scheme 1).[10] This has been isolated in ~50% yield as a pale blue crystalline solid, and its molecular structure has been established by single-crystal X-ray diffraction[11] and supported by elemental and thermal analyses and IR spectroscopy.[10]

The triclinic structure of **1** (Figure 1a) crystallizes within the *P*1 space group and is composed of two symmetry equivalent Cu1 atoms and two tetradentate bis-deprotonated μ-Htea(2−) ligands, two symmetry nonequivalent Mg1 and Mg2 atoms, one μ_6-pyromellitate(4−) ligand, and six coordinated (two at Mg1 and four at Mg2 atoms) and six crystallization water molecules per formula unit. The five-coordinate Cu1 atoms adopt rather distorted $\{CuNO_4\}$ square-pyramidal environments, filled by the μ-O1, O3, and N1 atoms of μ-Htea [Cu1−O1 1.963(2), Cu1−O3 1.950(2), Cu1−N1 2.003(2) Å] and the O4 atom of μ_6-pma [Cu1−O4 1.933(2) Å] in basal sites, whereas the remaining O2 atom of μ-Htea [Cu1−O2 2.270(2) Å] is located in the apical position. The six-coordinate Mg1 atom shows a distorted $\{MgO_6\}$ octahedral geometry occupied by the symmetry generated pairs of μ-O1, O5, and O6 atoms [Mg1−O1 2.040(2), Mg1−O5 2.047(2), Mg−O6 2.123(2) Å] from μ-Htea, μ_6-pma, and aqua ligands, respectively. The Mg2 atom also exhibits a distorted $\{MgO_6\}$ octahedral environment completed by the two O7 atoms from μ_6-pma [Mg2−O7 2.059(2) Å], as well as by the symmetry generated pairs of the O9 and O10 aqua ligands [Mg2−O9 2.062(2), Mg2−O10 2.061(2) Å], thus forming the 2-connected aqua-magnesium linkers. The Mg1 atoms act as the 4-connected nodes, which, along with the O4−C7−O5 carboxylate groups of μ_6-pma, assemble two adjacent Cu(Htea) moieties into a heterometallic Cu_2Mg cluster core $[Cu_2Mg(\mu\text{-O})_2(\mu\text{-COO})_2]^-$ (Figure 1b), an unprecedented character of which is supported by a search in the CSD.[4] The latter also reveals that compounds incorporating a simple Cu−O−Mg−O−Cu structural fragment are unexpectedly limited to only two examples,[12] which, however, are not coordination polymers. In **1**, the Cu_2Mg cluster cores are further interlinked with the μ_6-pma and Mg2 linkers, generating 1D ~pma−Cu_2Mg−pma−Mg~ chain motifs (Figure 1c). These are simultaneously pillared by the second two carboxylate groups of μ_6-pma, giving rise to an infinite 2D metal−organic layer (Figures 1d and S3). Each layer in **1** can also be described as a "rhombic grid" network[13] composed of "windows" formed by two Cu_2Mg cores, two Mg2 linkers, and four pyromellitate spacers (Figure S1 of the Supporting Information).

To get a deeper understanding of the 2D layered structure of **1**, we have carried out its topological analysis by applying the concept of the simplified underlying net[14] and using the TOPOS software package.[15] Hence, by contracting the Cu(Htea) and μ_6-pma moieties to their centroids, and omitting all H_2O ligands from the Mg atoms, the network of **1** can be described as an underlying net (Figure 2a,b), constructed from the 2-connected Cu(Htea) and Mg2 linkers, as well as the formally 6-connected pma and 4-connected Mg1 nodes. The latter are better treated as the 4-connected (pma) and 2-connected (Mg1) nodes due to the collinearity of some bonds between them.[15] The topological analysis of the resulting net discloses a binodal 2,4-connected network with the new topology described by the point symbol of $(6^4{\cdot}8{\cdot}10)(6)$, wherein the notations $(6^4{\cdot}8{\cdot}10)$ and (6) correspond to the pma and Mg1 nodes, respectively. Although 2,4-connected networks are known,[16] the present type of topology has not been documented previously.[4,15,17] To match this topology with one of the common topological types encountered in 2D coordination polymers,[14,15,17] the metal−organic network of **1** can be further simplified by considering the heterotrimetallic $[Cu_2Mg(\mu\text{-Htea})_2(H_2O)_2]^{2+}$ blocks as the 2-connected cluster linkers. Given the presence of the 2-connected Mg2 linkers and 4-connected pma nodes, the resulting uninodal 4-connected 2D net features the **sql** (Shubnikov tetragonal plane net) topology, with the point symbol of $(4^4{\cdot}6^2)$ (Figure 2c). It should be noted that a number of coordination polymers with the **sql** nets have been identified in recent years.[18]

Furthermore, the packing pattern of **1** along the *c* axis reveals that the neighboring 2D layers are repeated every 10.4720(3) Å (the *a* unit cell dimension), also being mutually interdigitated and held together, via direct intermolecular H-bonds [O2−H2O···O3^{vi} 2.520(3) Å], into an infinite 3D supramolecular framework (Figures 3a and S2). Hence, the H-bonds assemble the Htea moieties from adjacent 2D layers into the dimeric $(Htea)_2$ blocks that can be considered as the 4-connected nodes, which, along with the 4-connected Mg2 and 6-connected pma nodes, as well as the Cu1 and Mg2 linkers, construct a binodal 4,6-connected 3D network. This supramolecular net (Figures 3b and S4) features the new topology with the point symbol of $(3^2{\cdot}6^{10}{\cdot}7^2{\cdot}8)(3^2{\cdot}6^3{\cdot}7)_2$, wherein the notations $(3^2{\cdot}6^{10}{\cdot}7^2{\cdot}8)$ and $(3^2{\cdot}6^3{\cdot}7)$ correspond to pma and the topologically equivalent $(Htea)_2$/Mg1 nodes, respectively.

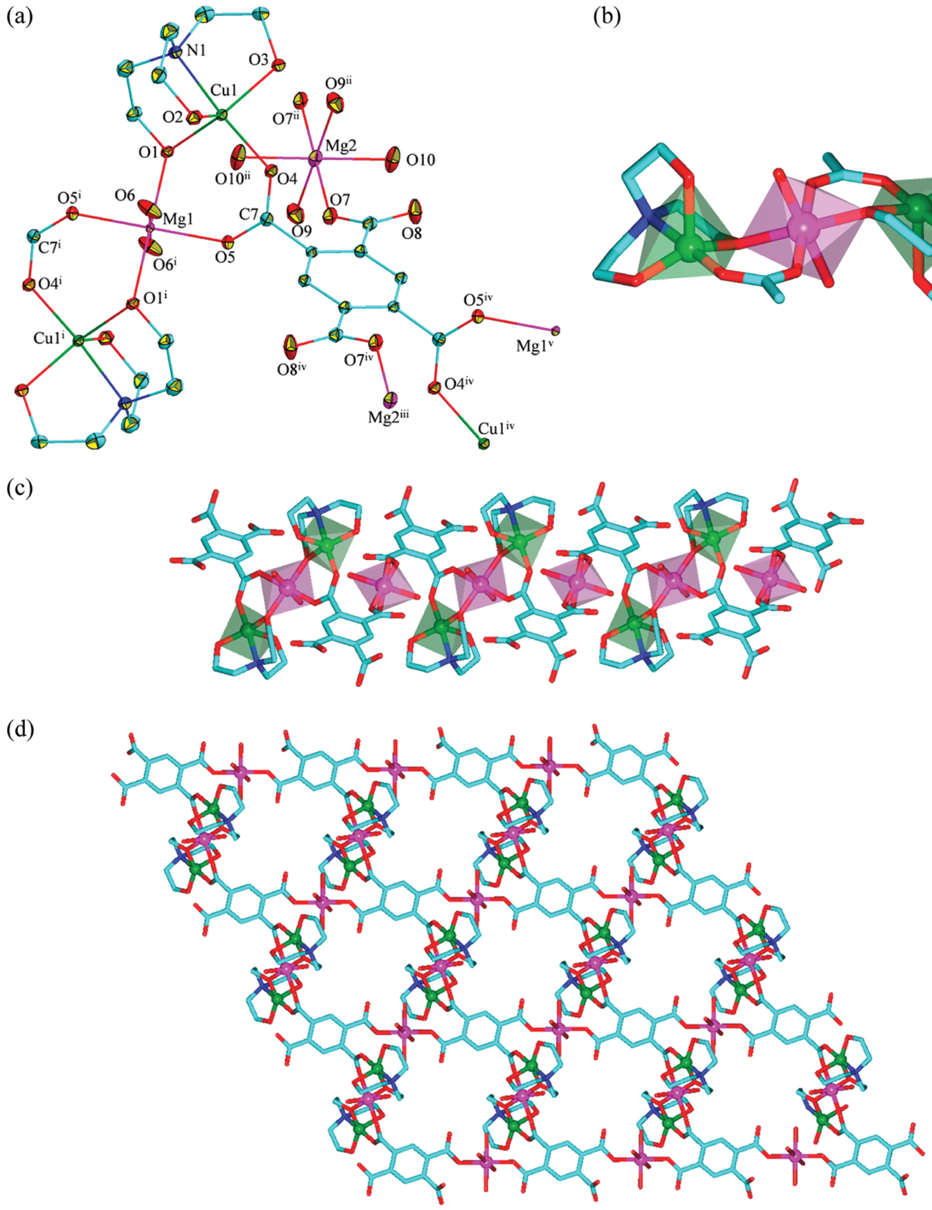


Figure 1. Structural fragments of **1** showing: (a) ellipsoid plot (50% probability) with partial atom labeling scheme, (b) heterometallic Cu_2Mg core with polyhedral representation of the coordination environments around the Cu1 and Mg1 atoms, (c) 1D ~pma−Cu_2Mg−pma−Mg~ chain motif, and (d) infinite 2D metal−organic layer. H atoms and crystallization H_2O molecules are omitted for clarity. Color codes: Cu balls (green), Mg balls (magenta), N (blue), O (red), C (cyan). Selected distances (Å): Cu1−O1 1.963(2), Cu1−O2 2.270(2), Cu1−O3 1.950(2), Cu1−O4 1.933(2), Cu1−N1 2.003(2), Mg1−O1 2.040(2), Mg1−O5 2.047(2), Mg1−O6 2.123(2), Mg2−O7 2.059(2), Mg2−O9 2.062(2), Mg2−O10 2.061(2), Cu1···Mg1 3.4693(5), Cu1···$Cu1^{i}$ 6.9386(7), Cu1···Mg2 4.4437(2), Mg1···Mg2 5.5295(2), Mg1···$Mg1^{v}$ 11.2635(3), Mg2···$Mg2^{iii}$ 11.2402(6). Hydrogen bonds [Å, deg]: within a 2D layer: O6−H6D···O2 [2.679(3), 173.6], O9−H9A···$O3^{ii}$ [2.637(3), 165.5], O10−H10A···$O1^{ii}$ [2.763(3), 157.3], O10−H10B···O8 [2.706(3), 154.4]; interlayer: O2−H2O···$O3^{vi}$ [2.520(3), 170.8]. Symmetry operators: (i) $2 - x, -y, 1 - z$; (ii) $2 - x, -y, 2 - z$; (iii) $-1 - x, -1 - y, -1 + z$; (iv) $1 - x, -1 - y, 1 - z$; (v) $-1 + x, -1 + y, z$; (vi) $1 - x, -y, 1 - z$.

In pursuit of our interest in the use of copper coordination polymers in oxidation catalysis,[5a,b,6a,7] we have tested the activity of **1** in the mild hydrocarboxylation of C_n alkanes into C_{n+1} carboxylic acids. These reactions were run following our recently developed alkane hydrocarboxylation protocol,[19] namely by reacting various C_5−C_9 linear and C_5−C_8 cyclic alkanes with carbon monoxide, water, and potassium peroxodisulfate, in neutral H_2O/MeCN medium, at low temperature (60 °C) for 4 h, and in the presence of **1** (Scheme 2). Although **1** is insoluble in H_2O/MeCN medium, it acts as a homogeneous catalyst precursor generating soluble catalytically active species upon the treatment with $K_2S_2O_8$ and CO. All the product yields are given in molar % based on alkanes, and the obtained results are summarized in Table 1. The reactions using the linear alkane substrates result in the single-pot formation of three or four isomeric acid products (Table 1, entries 1−5). Among them, the branched acids derived from the carboxylations at different secondary carbon atoms within the alkane chain are the major products, while the corresponding linear (fatty) acids are only generated in minor amounts (<1% yield). All the secondary C atoms are carboxylated without a considerable preference to any particular one, as attested by the regioselectivity[20] parameters (normalized for the relative number of H atoms) of C(1)/C(2)/C(3) = 1:36:33

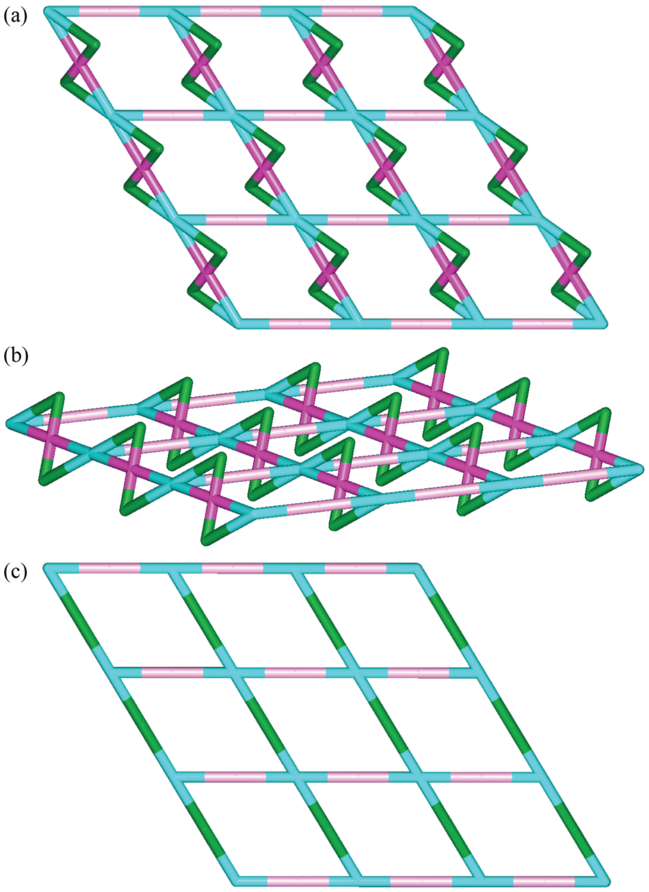


Figure 2. Topological representations of the simplified underlying 2D network in **1**: front (a) and side (b) views of the topologically unique binodal 2,4-connected net with the point symbol of $(6^4 \cdot 8 \cdot 10)(6)$; (c) further simplified uninodal 4-connected net with the **sql** (Shubnikov tetragonal plane net) topology. Color codes: (a−c) centroids of 4-connected pma nodes (cyan), and 2-connected Mg2 linkers (pale pink); (a, b) 2-connected Mg1 nodes (magenta) and centroids of 2-connected Cu(Htea) linkers (green); (c) centroids of 2-connected $[Cu_2Mg(\mu\text{-Htea})_2(H_2O)_2]^{2+}$ cluster linkers (green).

(for *n*-C_5H_{12}) and C(1)/C(2)/C(3)/C(4) = 1:24:21:20 (for *n*-C_7H_{16}). The maximum total yield is achieved in the hydrocarboxylation of *n*-pentane (25%), followed by *n*-hexane (17%), *n*-heptane (15%), and *n*-octane (15%), whereas *n*-nonane (9%) is the least reactive alkane. In contrast to the linear alkanes, the transformations of the C_5−C_8 cyclic alkanes result in only one carboxylic acid product (Table 1, entries 6−9) due to the presence of a single type of carbon atoms in these substrates. The maximum yields of cycloalkanecarboxylic acids are obtained in the reactions with cyclopentane (40%) and cyclohexane (28%), followed by cycloheptane (21%) and cyclooctane (14%), thus indicating a declining trend on increasing the size of the cycloalkane ring. The effect of time has been studied in the hydrocarboxylation of cyclohexane as a model substrate, showing that the typical reaction time of 4 h has been quite reasonable, since rather high yields of cyclohexanecarboxylic acid are already achieved after 2 h of the reaction (Figure S6 and Table S2 of the Supporting Information). The formation of the cyclic ketones and alcohols (oxidation products) in up to 13% overall yields also takes place when using cycloalkanes as substrates, while the yields of the oxidation products were negligible (typically below 1%) in the reactions of linear alkanes. The achieved herein yields of carboxylic acids are very high considering the exceptional inertness of alkanes[21] and the fact that the present hydrocarboxylations undergo at a very mild temperature (60 °C), in aqueous acid-solvent-free medium and involve C−H bond cleavage and C−C bond formation.

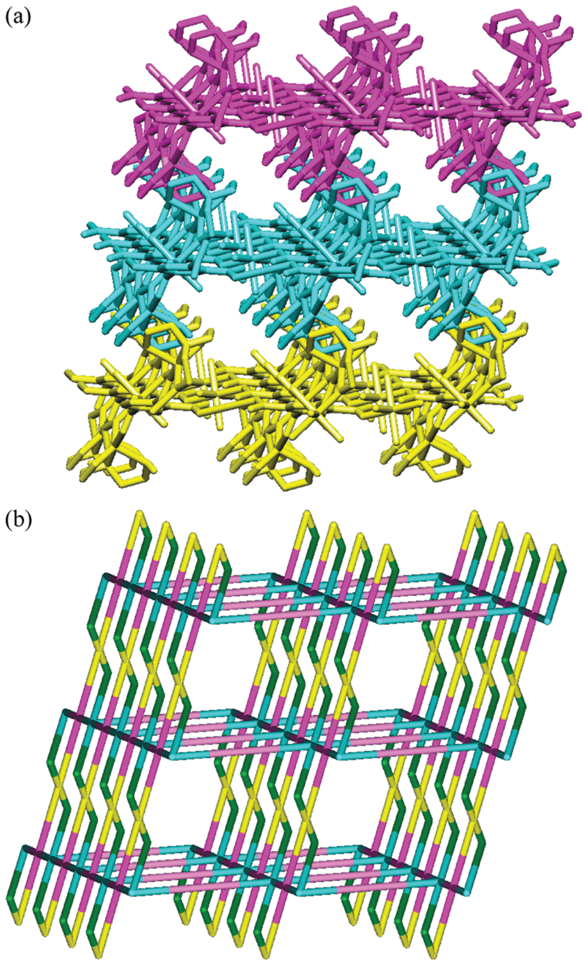
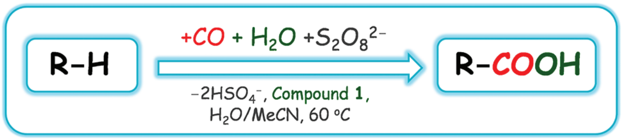


Figure 3. Structural fragments of **1**: (a) 3D supramolecular framework formed via the direct H-bonding linkage [O2−H2O···O3^{vi} 2.520(3) Å] of three adjacent interdigitated 2D layers represented by different colors (H atoms and crystallization H_2O molecules are omitted for clarity); (b) topological representation of the underlying binodal 4,6-connected net with an unprecedented topology. Color code: centroids of 6-connected pma (cyan) and 4-connected $(Htea)_2$ nodes (yellow), 4-connected Mg1 nodes (magenta), 2-connected Mg2 (pale pink) and Cu1 (green) linkers.

Scheme 2. Mild Single-Pot Hydrocarboxylation of C_n Alkanes into C_{n+1} Carboxylic Acids



In conclusion, the present work has widened the still very limited family of the heterometallic Cu^{II}/Mg coordination polymers to a new example, $[Cu_2Mg_2(\mu\text{-Htea})_2(\mu_6\text{-pma})(H_2O)_6]_n \cdot 6nH_2O$ (**1**), which shows a number of remarkable structural features, namely concerning its unprecedented heterotrimetallic $[Cu_2Mg(\mu\text{-O})_2(\mu\text{-COO})_2]^-$ core, and an identification of the new topologies in the binodal 2,4- or 4,6-connected 2D coordination or 3D supramolecular underlying networks,

Table 1. Single-Pot Hydrocarboxylation of C_n Alkanes into C_{n+1} Carboxylic Acids Catalyzed by 1[a]

entry	alkane	carboxylic acid product (yield, %)[b]	total yield (%)[c]
1	n-C_5H_{12}	2-methylpentanoic (16.8), 2-ethylbutanoic (7.6), hexanoic (0.7)	25.1
2	n-C_6H_{14}	2-methylhexanoic (7.8), 2-ethylpentanoic (8.3), heptanoic (0.5)	16.6
3	n-C_7H_{16}	2-methylheptanoic (6.5), 2-ethylhexanoic (5.6), 2-propylpentanoic (2.7), octanoic (0.4)	15.0
4	n-C_8H_{18}	2-methyloctanoic (5.0), 2-ethylheptanoic (5.1), 2-propylhexanoic (4.4), nonanoic (0.3)	14.8
5	n-C_9H_{20}	2-methylnonanoic (3.1), 2-ethyloctanoic (2.5), 2-propylheptanoic (2.3), 2-butylhexanoic (1.1), decanoic (0.2)	9.2
6	C_5H_{10}	cyclopentanecarboxylic (39.3), one/ol (4.3)[d]	43.6
7	C_6H_{12}	cyclohexanecarboxylic (28.1), one/ol (2.1)[d]	30.2
8	C_7H_{14}	cycloheptanecarboxylic (20.9), one/ol (6.5)[d]	27.4
9	C_8H_{16}	cyclooctanecarboxylic (13.7), one/ol (12.5)[d]	26.2

[a] Reaction conditions: alkane (1.0 mmol), $p(CO) = 20$ atm (1 atm = 0.266 mmol); compound **1** (4.0 μmol); $K_2S_2O_8$ (1.5 mmol). H_2O (2.0 mL)/MeCN (4.0 mL); 60 °C, 4 h, 13.0 mL autoclave. [b] Moles of product/100 moles of alkane. [c] Yield of all products. The following regioselectivity parameters C(1)/C(2)/C(3)/C(n) (normalized for the relative number of H atoms at different positions of linear alkane chains) were obtained: 1:36:33 (n-C_5H_{12}), 1:23:25 (n-C_6H_{14}), 1:24:21:20 (n-C_7H_{16}), 1:25:25:22 (n-C_8H_{18}), and 1:23:19:17:16 (n-C_9H_{20}). [d] one/ol = overall yield of cyclic ketones and alcohols (products of oxidation).

respectively. Besides, compound **1** has been applied as an efficient and versatile catalyst precursor for the mild single-pot hydrocarboxylation of inert C_n alkanes into the corresponding C_{n+1} carboxylic acids, thus extending the limited application of copper−organic networks in oxidation catalysis. Further research toward the exploration of the aqueous medium self-assembly protocol as a convenient synthetic tool for the design of new functional heterometallic coordination polymers is currently in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Materials and methods, refinement details for X-ray analysis, procedure for alkane hydrocarboxylation studies, supporting references, additional structural representations (Figures S1−S4), results of thermal analysis (Figure S5, Table S1), additional catalytic tests (Figure S2, Table S2), and crystallographic file in CIF format for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: kirillov@ist.utl.pt (A.M.K.); pombeiro@ist.utl.pt (A.J.L.P.). Phone: +351 218419207/37. Fax: +351 218464455.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Foundation for Science and Technology (FCT) (Projects PTDC/QUI-QUI/121526/2010, PTDC/QUI-QUI/102150/2008, and PEst-OE/QUI/UI0100/2011), Portugal, as well as its "Science 2007" program.

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(10) *Synthesis and analytical data of* **1**: To an aqueous solution (10.0 mL) of $Cu(NO_3)_2 \cdot 2.5H_2O$ (1.00 mmol) were added triethanolamine (1.00 mmol, 130 μL) and an excess of $Mg(OH)_2$ (0.5 g, 8.65 mmol) in this order, and with continuous stirring in air at room temperature (rt, ~25 °C). Pyromellitic acid (0.50 mmol, 127 mg) was dissolved in an aqueous solution (2.0 mL) of LiOH (2.0 mmol, 46 mg) and then added to the reaction mixture. This was stirred for 1 day and filtered off; the filtrate was left in a beaker to evaporate in air at rt. Pale blue crystals (including those of X-ray quality) were formed in 1−2 weeks

and then collected and dried in air to furnish **1** in ~50% yield, based on copper nitrate. **1** is insoluble in water and common organic solvents. $C_{22}H_{52}Cu_2Mg_2N_2O_{26}$ (936.3) Calcd: C 28.22, N 2.99, H 5.60. Found: C 27.91, N 3.10, H 5.39. IR (KBr, selected bands): 3450 (s br) ν(OH), 2946 (w), 2913 (w) and 2864 (w) ν(CH), 1620 (vs) and 1496 (w) ν_{as}(COO), 1417 (m sh) and 1394 (s) ν_s(COO), 1042 (s), 902 (m), 611 (m) and 580 (m) cm^{-1}.

(11) *Crystal data*: **1**: $C_{11}H_{26}CuMgNO_{13}$, $M = 468.18$, $\lambda = 0.71073$ Å (Mo Kα), $T = 120(2)$ K, triclinic, space group $P1$, $a = 10.4720(3)$, $b = 10.5610(3)$, $c = 11.0590(4)$ Å, $\alpha = 96.271(2)$, $\beta = 114.843(2)$, $\gamma = 115.2440(10)°$, $V = 939.88(5)$ Å^3, $Z = 2$, $D_c = 1.654$ g/cm^3, $\mu = 1.262$ mm^{-1}, 18184 reflections collected, 4287 unique, $I > 2\sigma(I)$ ($R_{int} = 0.0363$), $R_1 = 0.0408$, $wR_2 = 0.1003$, GOF 1.022.

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