

Self-Assembled Two-Dimensional Water-Soluble Dipicolinate Cu/Na Coordination Polymer: Structural Features and Catalytic Activity for the Mild Peroxidative Oxidation of Cycloalkanes in Acid-Free Medium

Marina V. Kirillova,^[a] Alexander M. Kirillov,^{*[a]} M. Fátima C. Guedes da Silva,^[a,b] and Armando J. L. Pombeiro^{*[a]}

Keywords: Self-assembly / N,O ligands / Supramolecular chemistry / C–H activation / Homogeneous catalysis

The new water-soluble 2D Cu/Na coordination polymer $[\text{Cu}(\mu\text{-dipic})_2\{\text{Na}_2(\mu\text{-H}_2\text{O})_4\}]_n \cdot 2n\text{H}_2\text{O}$ (**1**) has been synthesized by self-assembly in aqueous medium from copper(II) nitrate, dipicolinic acid (H_2dipic) and sodium hydroxide in the presence of triethanolamine. It has been characterized by IR spectroscopy, FAB⁺-MS, elemental and single-crystal X-ray diffraction analyses, the latter featuring a layered 2D metal–organic structure that is extended to a 3D supramolecular assembly by extensive hydrogen bonding between adja-

cent layers and involving crystallization water molecules. Compound **1** has been shown to act as a catalyst precursor for the peroxidative oxidation of cyclohexane and cyclopentane to the corresponding cyclic ketones and alcohols by aqueous H_2O_2 in MeCN solution and in the absence of acid additives.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2008)

Introduction

Pyridine-2,6-dicarboxylic acid (dipicolinic acid, H_2dipic) is a well-known, versatile N,O-chelator in coordination chemistry,^[1] which, apart from forming a rich family of mono- and polynuclear complexes,^[2] has also been a convenient ligand for the design of various polymeric metal–organic frameworks and supramolecular assemblies.^[2,3] In particular, among an array of transition-metal compounds derived from dipicolinic acid, copper dipicolinates represent the major part,^[2] exhibiting interesting properties and applications in molecular magnetism, crystal engineering and bioinorganic and aqueous chemistry.^[4] Nevertheless, although dipicolinic acid features a recognized biological function,^[4d,5] to the best of our knowledge, the application of its copper compounds as bioinspired catalysts have not yet been reported.

We have recently developed various interfacing research lines with relevance to self-assembly synthetic procedures in aqueous medium and synthesis of copper complexes, coordination polymers and hydrogen bonded supramolecular frameworks,^[3b,4d,6] as well as their application in the mild catalytic transformations of alkanes,^[6a,d–h] crystal engineer-

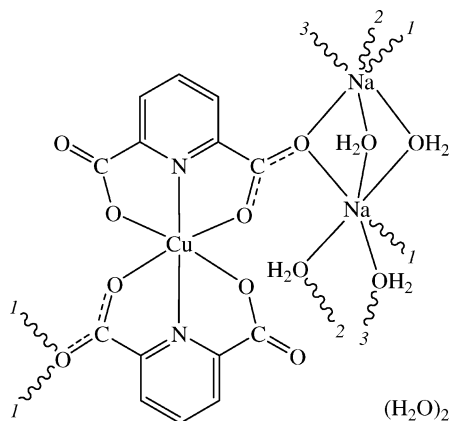
ing^[3b,4d,6a,b,d–f] and molecular magnetism.^[6b,6e] Being also focused on the preparation of water-soluble compounds,^[3b,6c,6g] we have synthesized a series of heteronuclear aqua dipicolinate complexes of Co, Ni, Cu and Zn,^[4d] as well as a 2D Cu/Na coordination polymer^[6f] constructed from copper triethanolamine and aqua–sodium building blocks and pyromellitate linkers. This compound appeared to be the first highly water-soluble Cu coordination polymer. As a continuation and potential merging of these studies, the current work aims at the synthesis of a related Cu/Na polymeric compound derived from dipicolinic acid and at probing its catalytic potential towards the peroxidative oxidation of cycloalkanes, thus mimicking the multicopper particulate methane monooxygenase (pMMO).^[7]

Results and Discussion

The combination in aqueous solution, at ambient temperature and in air, of copper(II) nitrate, triethanolamine (H_3tea), sodium hydroxide and dipicolinic acid gives rise to the formation by self-assembly of the new water soluble polymeric product $[\text{Cu}(\mu\text{-dipic})_2\{\text{Na}_2(\mu\text{-H}_2\text{O})_4\}]_n \cdot 2n\text{H}_2\text{O}$ (**1**, Scheme 1). It has been isolated as a light blue crystalline solid and characterized^[8] by IR spectroscopy, FAB⁺-MS, elemental and single-crystal X-ray diffraction analyses.^[10] Compound **1** does not bear triethanolamine moieties, but the use of H_3tea is crucial for its synthesis, since, in the absence of H_3tea , another product, $[\text{Cu}(\text{H}_2\text{O})_5\text{Cu}(\text{dipic})_2] \cdot 2\text{H}_2\text{O}$,^[4d,13] is formed. Hence, triethanolamine appears to behave as a template towards the generation of **1**.

[a] Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, TU Lisbon, Av. Rovisco Pais, 1049-001 Lisbon, Portugal
Fax: +351-21-846-4455
E-mail: pombeiro@ist.utl.pt
kirillov@ist.utl.pt

[b] Universidade Lusófona de Humanidades e Tecnologias, ULHT Lisbon, Av. do Campo Grande, 376, 1749-024 Lisbon, Portugal



Scheme 1. Schematic representation of **1** (numbers correspond to extensions of the polymeric network).

The IR spectrum of **1** exhibits a strong and broad band in the 3700–2800 cm^{-1} region (max. at 3407 cm^{-1}) due to the $\nu(\text{H}_2\text{O})$ vibrations associated with both aqua–sodium units and crystallization water molecules. The broad character of this band results in the overlapping of weak $\nu(\text{CH})$ vibrations and is indicative of an extensive hydrogen bonding. Other characteristic bands correspond to very strong ν_{as} and ν_{s} vibrations (with maxima at 1621 and 1383 cm^{-1} , respectively) of COO groups of dipic ligands.^[3b,4d] The positive FAB⁺-MS spectrum of **1** allows the detection of the following fragments: $[\text{Cu}(\text{dipic})_2 + 3\text{Na}]^+$ ($m/z = 462$), $[\text{Cu}(\text{dipic})_2\text{Na}_2 + \text{H}]^+$ ($m/z = 440$) and $[\text{Cu}(\text{dipic})_2 + 3\text{H}]^+$ ($m/z = 396$), all in accord with the expected isotopic patterns.

The molecular structure of **1** (Figure 1, Figure 2) features an infinite nonplanar 2D metal–organic network constructed from monomeric $[\text{Cu}(\text{dipic})_2]^{2-}$ units and polymeric $\{[\text{Na}_2(\mu\text{-H}_2\text{O})_4]^{2+}\}_n$ chains, alternating every 9.7626(12) Å (the unit cell dimension a). The geometry around the Cu1 atoms is significantly distorted octahedral [the main deviation involves the O11–Cu1–O21 angle of 156.43(5)°] and is formed by two nearly planar N,O,O -dipicolinate ligands that adopt an arrangement in which they are almost perpendicular to each other (Figure 1). The connection of the $[\text{Cu}(\text{dipic})_2]^{2-}$ units with aqua–sodium moieties is realized through the O12 carboxylate atoms, simultaneously bridging the Na1 [2.3539(15) Å] and Na2 [2.4726(15) Å] atoms and contributing to their distorted octahedral geometry. The octahedral geometry is completed by two symmetry-equivalent O1 [avg. Na–O1 2.409(2) Å] and O3 [avg. Na–O3 2.483(2) Å] bridging water molecules, resulting in the generation of repeated up-down alternate $[\text{Na}_2(\mu\text{-O}_{\text{carboxylate}})(\mu\text{-H}_2\text{O})_2]$ triangular bipyramid-like cages of a rather unusual type.^[14] The Na1...Na2 separation within those cages is 3.2640(5) Å, and the representative Na–O–Na and O–Na–O angles are listed in Figure 1. In general, most of the bonding parameters in **1** are comparable to those reported for other polymeric dipicolinate compounds bearing either $[\text{Cu}(\text{dipic})_2]^{2-}$ [4a,4e,4h] or $[\text{Na}(\text{H}_2\text{O})_n]^+$ [4h,15] moieties.

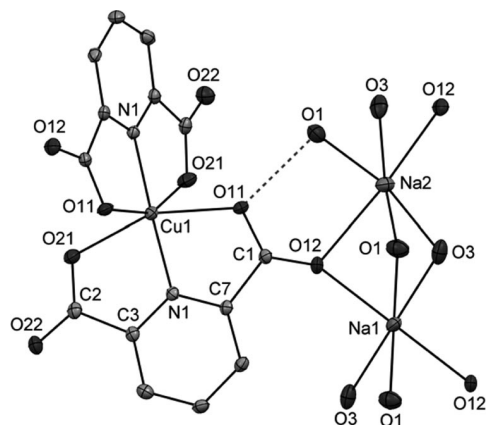


Figure 1. Structural fragment of **1** with partial atom labelling scheme and intramolecular hydrogen bond (dashed line). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and crystallization water molecules are omitted for clarity. Symmetry operators were used to generate equivalent atoms. Selected bond lengths [Å] and angles [°]: Cu1–O11 2.1840(16), Cu1–O21 2.2095(16), Cu1–N1 1.9278(17), Na1–O1 2.377(2), Na1–O3 2.5713(19), Na1–O12 2.3539(15), Na2–O1 2.441(2), Na2–O3 2.393(2), Na2–O12 2.4726(15), O11–Cu1–O21 156.43(5), O11–Cu1–N1 78.65(6), O21–Cu1–N1 77.85(6), Na1–O1–Na2 85.28(8), Na1–O3–Na2 82.13(5), Na1–O12–Na2 85.07(5), O1–Na2–O12 74.39(6), O3–Na2–O12 76.66(6), O1–Na2–O3 88.29(7). Hydrogen bond D–H...A: for O1–H1A...O11ⁱ $d(\text{D}\cdots\text{A}) = 2.898(2)$ Å; $\angle(\text{DHA}) = 155(3)^\circ$ [symmetry code: (i) $-x, y, 1/2 - z$].

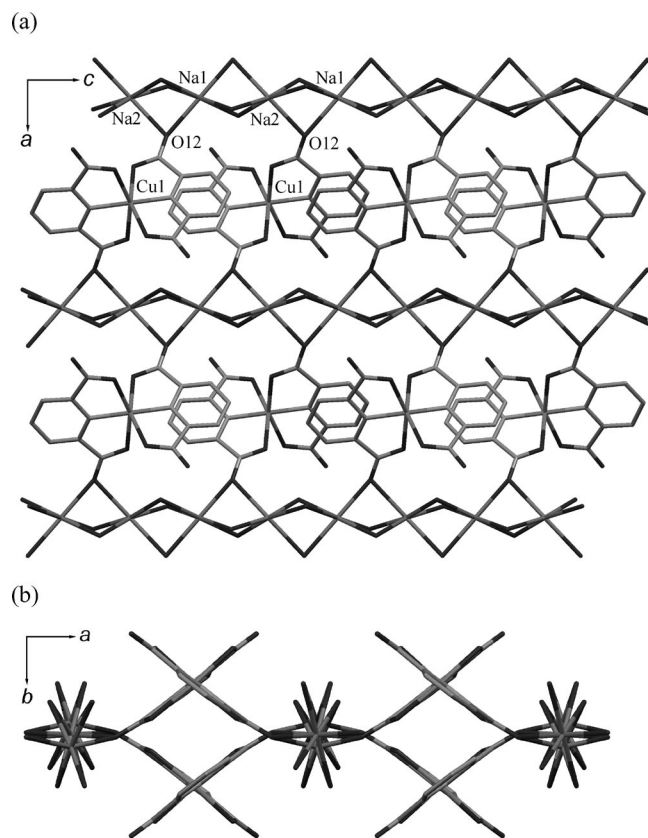


Figure 2. Fragment of the crystal packing diagram of **1** along the b axis (a) and the c axis (b) showing front (a) and side (b) views of one 2D metal–organic layer. Hydrogen atoms and crystallization H_2O molecules are omitted for clarity.

Intramolecular O1–H1A...O11ⁱ [2.898(2) Å] and intermolecular O3–H3A...O22ⁱⁱ [2.841(2) Å] hydrogen bonds (the symmetry codes are those of Figure 1 and Figure 3) between the coordinated water molecules (O1, O3) and carboxylate groups (O11, O22) provide an additional linkage of [Cu(dipic)₂]²⁻ and {Na₂(μ-H₂O)₄}²⁺_n building blocks, thus contributing to the reinforcement of 2D metal–organic layers and their direct interconnection, respectively. The neighbouring layers alternate every 9.7626(12) Å (the unit cell dimension *b*). In addition, the crystallization water molecules O4 (two per formula unit) are located between layers and participate in the formation of four intermolecular hydrogen bonds (donating H atoms to carboxylate O21 and O22 atoms, and accepting from O3 and O1 water ligands), thus giving rise to an extensive indirect linkage of adjacent 2D layers and generation of a 3D supramolecular assembly (Figure 3).

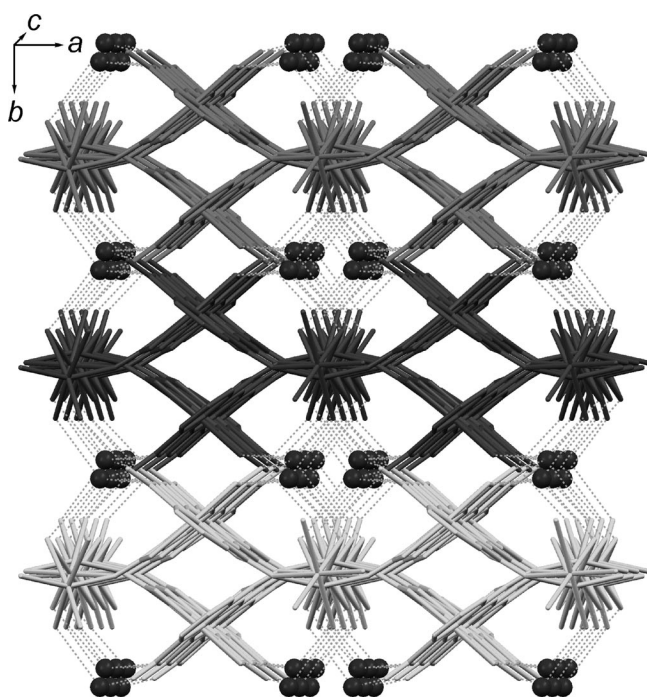
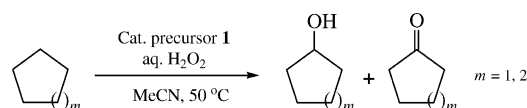


Figure 3. Fragment of the crystal packing diagram of **1** (rotated view along the *c* axis) representing the relative arrangement of three metal–organic layers shown by different shades of grey, which are extensively interlaced by intermolecular hydrogen bonds (dotted lines) between adjacent layers (direct linkage) and involve intercalated crystallization water molecules (represented as balls; indirect linkage), resulting in the formation of a 3D supramolecular assembly. Hydrogen atoms are omitted for clarity. Hydrogen bonds D–H...A [*d*(D...A) [Å]; ∠(DHA) [°]]: O3–H3A...O22ⁱⁱ {2.841(2); 167(4)}, O3–H3B...O4ⁱⁱⁱ {2.928(3); 164(3)}, O4–H4A...O21^{iv} {2.946(3); 168(3)}, O4–H4B...O22^v {2.798(3); 170(3)}, O1–H1B...O4 {3.095(3); 167(5)} [symmetry codes: (ii) $-1 + x, 1 + y, z$; (iii) $x, 1 + y, z$; (iv) $1 - x, y, 1/2 - z$; (v) $1 - x, 1 - y, 1 - z$]. For an atom labelling scheme, see Figure 1.

In pursuit of our interest on the mild oxidation of alkanes catalyzed by Cu^{II} centres,^[6a,6d–6h] we have preliminarily screened the catalytic potential of **1** for the peroxidative oxidation (i.e., by using a peroxide as an oxidant) of cyclohexane and cyclopentane by aqueous H₂O₂ in MeCN

solution at 50 °C to the corresponding cyclic alcohols and ketones (Scheme 2).^[16] Thus, **1** acts as a catalyst precursor in these transformations, leading to the overall product yields of 11.1 and 9.9% (molar yields based on cycloalkanes) for cyclohexane and cyclopentane oxidation, respectively. Cyclic alcohols (cyclohexanol and cyclopentanol) are the major final products after the treatment of the final reaction mixtures with triphenylphosphane, following a method developed by Shul'pin.^[17] The observed pronounced increase of the alcohol/ketone molar ratio upon this treatment with PPh₃ indicates the formation of cycloalkylhydroperoxides (ROOH) as the main primary products of the cycloalkane (RH) oxidation. The quantitative reduction of ROOH by PPh₃ to the corresponding cyclic alcohols (ROH) results in the elevated yields of the latter, with concomitant reduction of the amount of ketone.^[17]



Scheme 2.

For cyclohexane oxidation, the above-mentioned yield of 11.1% corresponds to a turnover number (TON, mol of products/mol of **1**) of 15, which can be increased up to 55 (still with a reasonable overall product yield of 6.0%) upon modifying some reaction parameters.^[18] It should be noted that the catalyst precursor **1** is active in the absence of any acid additive, while the addition of only 5 equiv. of HNO₃ relative to **1** leads to a full suppression of its catalytic activity.^[16] Such behaviour contrasts with those of our previously reported Cu^{II} systems,^[6a,6d–6h] for the peroxidative oxidation of cycloalkanes, which exhibit high activity only in the presence of an acid additive. Hence, the ability of **1** to catalyze cycloalkane oxidations in acid-free systems constitutes an important feature, presumably related to the dipicolinate environment around the Cu^{II} atom and to the aqueous solubility. As observed for other Cu^{II} catalytic systems,^[6a,6d–6h] the introduction into the reaction mixture of a radical trap (CBrCl₃, BHT or Ph₂NH)^[16] results in an almost full suppression of the activity of **1**. This behaviour, along with the formation of cycloalkyl hydroperoxides (typical intermediates in radical-type reactions, as discussed below), supports a free-radical mechanism for the cycloalkane oxidation.

Aiming to obtain further mechanistic information, we have performed EPR measurements,^[19] which reveal similar spectral features of **1** in both the solid state and in aqueous solution, thus supporting the preservation of the [Cu(dipic)₂]²⁻ cores upon dissolution of the compound. However, the intensity of the EPR signal dramatically decreases (without a change in the *g* factor) upon treatment of an aqueous solution of **1** with hydrogen peroxide, thus suggesting the formation of a diamagnetic Cu^I species. The introduction of a high excess of H₂O₂, however, does not lead to the complete disappearance of the Cu^{II} EPR signal, on account of the reversibility of the Cu^{II} ↔ Cu^I transformation as expected for a catalytic cycle that may include the

following steps: (i) $\text{Cu}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Cu}^+ + \text{HOO}^\cdot + \text{H}^+$; (ii) $\text{Cu}^{2+} + \text{HOO}^\cdot \rightarrow \text{Cu}^+ + \text{H}^+ + \text{O}_2$; (iii) $\text{Cu}^+ + \text{H}_2\text{O}_2 \rightarrow \text{Cu}^{2+} + \text{HO}^\cdot + \text{HO}^\cdot$.^[20] These steps are in accord with the proposed free-radical mechanism of cycloalkane oxidation, which is further supported by the observed intense release of dioxygen and colour change (from pale blue to greenish yellow) on addition of hydrogen peroxide to an aqueous solution of **1**. Besides, the catalytic oxidation of cyclohexane under dinitrogen (keeping the other reaction conditions the same^[16]) results in a drop in the total product yield from 11.1 to 5.1%. This fact confirms also the involvement of atmospheric oxygen, by facilitating the generation of cycloalkylperoxyl ($\text{ROO}^\cdot$) radicals ($\text{R}^\cdot + \text{O}_2 \rightarrow \text{ROO}^\cdot$), which lead to the formation of cycloalkyl hydroperoxide primary products ($\text{ROO}^\cdot + \text{HOO}^\cdot \rightarrow \text{ROOH} + \text{O}_2$; and $\text{ROO}^\cdot + \text{RH} \rightarrow \text{ROOH} + \text{R}^\cdot$).^[17] It should also be noted that the activity of the heterometallic compound **1** is associated with copper ions, while sodium cations have no direct involvement in the observed catalysis.^[21]

Conclusions

We have prepared and fully characterized a novel 2D Cu/Na coordination polymer $[\text{Cu}(\mu\text{-dipic})_2\{\text{Na}_2(\mu\text{-H}_2\text{O})_4\}]_n \cdot 2n\text{H}_2\text{O}$, whose layered metal–organic network driven by aqua–sodium chains bears a rare $[\text{M}_2(\mu\text{-O}_{\text{carboxylate}})(\mu\text{-H}_2\text{O})_2]$ core and is further extended to a 3D supramolecular assembly by means of multiple hydrogen bonds and guest water molecules. This compound widens the still limited family^[6f] of water-soluble copper(II) coordination polymers. Being derived from the biologically relevant dipicolinate ligand,^[4d,5] it acts as a promising bioinspired catalyst precursor, related to the multicopper particulate methane monooxygenase (pMMO),^[7] for the mild peroxidative oxidation of cycloalkanes to give the corresponding cyclic alcohols and ketones, without requiring the presence of an acid promoter. Further research towards the detailed exploration of its catalytic potential and establishment of the mechanism will be pursued.

Acknowledgments

This work has been partially supported by the POCI 2010 (FEDER funded) and “Science 2007” programs of the Foundation for Science and Technology (FCT), Portugal. We gratefully thank Dr. João Paulo Telo (IST) for his help with the EPR measurements.

- [1] For a review, see: L. C. Nathan, *Trends Inorg. Chem.* **1993**, 3, 415.
- [2] See the Cambridge Structural Database (CSD, version 5.28, Jan. 2008): F. H. Allen, *Acta Crystallogr., Sect. B* **2002**, 58, 380.
- [3] a) S. X. Cui, Y. L. Zhao, B. Li, J. P. Zhang, Q. Liu, Y. Zhang, *Polyhedron* **2008**, 27, 671; b) M. V. Kirillova, A. M. Kirillov, M. F. C. Guedes da Silva, M. N. Kopylovich, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, *Inorg. Chim. Acta* **2008**, 361, 1728, and references cited therein; c) X. Q. Zhao, B. Zhao, Y. Ma, W. Shi, P. Cheng, Z. H. Jiang, D. Z. Liao, S. P. Yan, *Inorg. Chem.* **2007**, 46, 5832; d) B. Zhao, L. Yi, Y. Dai, X. Y. Chen, P. Cheng, D. Z. Liao, S. P. Yan, Z. H. Jiang, *Inorg. Chem.* **2005**,

- 44, 911; e) S. K. Ghosh, P. K. Bharadwaj, *Inorg. Chem.* **2004**, 43, 2293; f) S. K. Ghosh, P. K. Bharadwaj, *Inorg. Chem.* **2003**, 42, 8250.
- [4] a) N.-H. Hu, Z.-G. Li, J.-W. Xu, H.-Q. Jia, J.-J. Niu, *Cryst. Growth Des.* **2007**, 7, 15; b) S. I. Kirin, K. Ohr, H. P. Yennawar, C. M. Morgan, L. A. Levine, M. E. Williams, *Inorg. Chem. Commun.* **2007**, 10, 652; c) S. C. Manna, J. Ribas, E. Zangrando, N. R. Chaudhuri, *Inorg. Chim. Acta* **2007**, 360, 2589; d) M. V. Kirillova, M. F. C. G. da Silva, A. M. Kirillov, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, *Inorg. Chim. Acta* **2007**, 360, 506, and references cited therein; e) Y.-P. Cai, C.-Y. Su, G.-B. Li, Z.-W. Mao, C. Zhang, A.-W. Xu, B.-S. Kang, *Inorg. Chim. Acta* **2005**, 358, 1298; f) S. K. Ghosh, J. Ribas, P. K. Bharadwaj, *CrystEngComm* **2004**, 6, 250; g) B. Schmidt, J. Jiricek, A. Titz, G. F. Ye, K. Parang, *Bioorg. Med. Chem. Lett.* **2004**, 14, 4203; h) L. C. Nathan, T. D. Mai, *J. Chem. Crystallogr.* **2000**, 30, 509.
- [5] T. Douki, B. Setlow, P. Setlow, *Photochem. Photobiol. Sci.* **2005**, 4, 591, and references cited therein.
- [6] a) Y. Y. Karabach, A. M. Kirillov, M. Haukka, M. N. Kopylovich, A. J. L. Pombeiro, *J. Inorg. Biochem.* **2008**, 102, 1190; b) A. M. Kirillov, Y. Y. Karabach, M. Haukka, M. F. C. Guedes da Silva, J. Sanchiz, M. N. Kopylovich, A. J. L. Pombeiro, *Inorg. Chem.* **2008**, 47, 162; c) A. M. Kirillov, P. Smoleński, M. F. C. Guedes da Silva, A. J. L. Pombeiro, *Eur. J. Inorg. Chem.* **2007**, 2686; d) C. Di Nicola, Y. Y. Karabach, A. M. Kirillov, M. Monari, L. Pandolfo, C. Pettinari, A. J. L. Pombeiro, *Inorg. Chem.* **2007**, 46, 221; e) D. S. Nesterov, V. N. Kokozay, V. V. Dyakonov, O. V. Shishkin, J. Jezierska, A. Ozarowski, A. M. Kirillov, M. N. Kopylovich, A. J. L. Pombeiro, *Chem. Commun.* **2006**, 4605; f) Y. Y. Karabach, A. M. Kirillov, M. F. C. G. da Silva, M. N. Kopylovich, A. J. L. Pombeiro, *Cryst. Growth Des.* **2006**, 6, 2200; g) A. M. Kirillov, M. N. Kopylovich, M. V. Kirillova, E. Y. Karabach, M. Haukka, M. F. C. G. da Silva, A. J. L. Pombeiro, *Adv. Synth. Catal.* **2006**, 348, 159; h) A. M. Kirillov, M. N. Kopylovich, M. V. Kirillova, M. Haukka, M. F. C. G. da Silva, A. J. L. Pombeiro, *Angew. Chem. Int. Ed.* **2005**, 44, 4345.
- [7] a) R. L. Lieberman, A. C. Rosenzweig, *Nature* **2005**, 434, 177; b) S. I. Chan, V. C.-C. Wang, J. C.-H. Lai, S. S.-F. Yu, P. P.-Y. Chen, K. H.-C. Chen, C.-L. Chen, M. K. Chan, *Angew. Chem. Int. Ed.* **2007**, 46, 1992.
- [8] Synthesis of $[\text{Cu}(\mu\text{-dipic})_2\{\text{Na}_2(\mu\text{-H}_2\text{O})_4\}]_n \cdot 2n\text{H}_2\text{O}$ (**1**): To an aqueous solution (10.0 mL) containing $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (1.00 mmol, 233 mg) and HNO_3 (1.00 mmol) [the acid was added to avoid spontaneous hydrolysis of the metal salt] were added dropwise triethanolamine (1.00 mmol, 130 μL) and an aqueous solution (4.0 mL) of NaOH (160 mg, 4.00 mmol), and solid H_2dipic (84 mg, 0.50 mmol), in this order and with continuous stirring in air at ambient temperature. The resulting clear blue solution was stirred overnight, then passed through a filter, concentrated under reduced pressure to one half of its volume, and kept in a beaker in air at ambient temperature. Light blue X-ray quality crystals were formed in 2–3 weeks from a deep blue oily solution, then collected, gently wiped with a filter paper and dried in air to furnish compound **1** in ca. 70% yield based on H_2dipic . Compound **1** is soluble in H_2O ($S_{25^\circ\text{C}} \approx 15 \text{ mg mL}^{-1}$) and can be recrystallized from an aqueous solution in the original form. $\text{C}_{14}\text{H}_{18}\text{CuN}_2\text{Na}_2\text{O}_{14}$ (547.8): calcd. C 30.69, H 3.31, N 5.11; found C 30.28, H 3.04, N 5.09. FAB⁺-MS (*m*-nitrobenzylalcohol): $m/z = 462$ $[\text{Cu}(\text{dipic})_2 + 3\text{Na}]^+$, 440 $[\text{Cu}(\text{dipic})_2\text{Na}_2 + \text{H}]^+$, 396 $[\text{Cu}(\text{dipic})_2 + 3\text{H}]^+$. IR (KBr, selected bands): $\tilde{\nu} = 3407$ (vs. br) and 3108 (w sh) $\nu(\text{H}_2\text{O})$, 1685 (sh), 1621 (vs. br) and 1591 (sh) $\nu_{\text{as}}(\text{COO}) + \delta(\text{H}_2\text{O})$, 1421 (s) and 1383 (vs. br) $\nu_{\text{s}}(\text{COO})$, 1279 (s), 1186 (m), 1156 (w), 1081 (s), 1043 (w), 997 (w), 913 (s), 855 (w), 822 (m), 768 (s), 733 (s), 689 (m), 510 (m), 444 (w) and 420 (w) (other bands) cm^{-1} . All characterization procedures were performed with the instruments and according to the techniques previously described.^[9]

- [9] A. M. Kirillov, M. Haukka, M. V. Kirillova, A. J. L. Pombeiro, *Adv. Synth. Catal.* **2005**, 347, 1435.
- [10] X-ray crystal structure determination: X-ray data were collected with an Enraf–Nonius CAD4 diffractometer equipped with graphite monochromator and by using Mo- K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods with the SHELXS-97 program.^[11] A semiempirical absorption correction was applied.^[12] The structure was refined with the SHELXL-97 program.^[11] All hydrogen atoms were located. Crystal data for **1**: $C_{14}H_{18}CuN_2Na_2O_{14}$, $M = 547.82$, monoclinic, space group $P2_1/c$, $a = 9.7626(12) \text{ \AA}$, $b = 7.9756(10) \text{ \AA}$, $c = 12.9066(13) \text{ \AA}$, $V = 1004.9(2) \text{ \AA}^3$, $Z = 2$, $D_c = 1.811 \text{ g cm}^{-3}$, $F_{000} = 558$, $\mu = 1.210 \text{ mm}^{-1}$, $T = 293 \text{ K}$, 2026 reflections collected, 1624 reflections with $I > 2\sigma(I)$ ($R_{\text{int}} = 0.0217$), $\text{GoF} = 1.100$, $R_1 = 0.0281$, $wR_2 = 0.0736$. CCDC-683529 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [11] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, 64, 112.
- [12] A. C. T. North, D. C. Phillips, F. S. Mathews, *Acta Crystallogr., Sect. A* **1968**, 24, 351.
- [13] L. Wang, L. Duan, D. Xiao, E. Wang, C. Hu, *J. Coord. Chem.* **2004**, 57, 1079.
- [14] It is interesting to note that according to a search in the CSD,^[2] the encountered $[M_2(\mu\text{-O}_{\text{carboxylate}})(\mu\text{-H}_2\text{O})_2]$ core, with bridging carboxylate oxygen and two $\mu\text{-H}_2\text{O}$ molecules completing the coordination sphere of two metal (M) atoms, appears to be rarely observed [only 7 matches; CSD refcodes: ALOWUT (Ca), NOVJUD (Na), NOLGOK and RUHHUX (Ba), KAMYON, VENDUN01 and YEHBUJ (K)], in contrast to numerous structures (ca. 107 hits) bearing simpler $[M_2(\mu\text{-O}_{\text{carboxylate}})(\mu\text{-H}_2\text{O})]$ fragments.
- [15] a) C. Ma, C. Chen, F. Chen, X. Zhang, H. Zhu, Q. Liu, D. Liao, L. Li, *Bull. Chem. Soc. Jpn.* **2003**, 76, 301; b) J. Limburg, G. W. Brudvig, R. H. Crabtree, *J. Am. Chem. Soc.* **1997**, 119, 2761; c) Y. Dai, W. Shi, X.-J. Zhu, B. Zhao, P. Cheng, *Inorg. Chim. Acta* **2006**, 359, 3353; d) J. Chakraborty, H. Mayer-Figge, W. S. Sheldrick, P. Banerjee, *Polyhedron* **2006**, 25, 3138; e) C.-Z. Xie, B. Yu, X.-Q. Wang, R.-J. Wang, G.-Q. Shen, D.-Z. Shen, *J. Coord. Chem.* **2006**, 59, 2005.
- [16] Peroxidative oxidation of cyclohexane and cyclopentane: The catalyst precursor **1** (5.0 mg, 9.2 μmol), used as a solid, was mixed with the cycloalkane (1.25 mmol), CH_3NO_2 (internal standard for GC analysis, 0.50 mL of its 1.4 M solution in MeCN), acetonitrile (4.20 mL) and H_2O_2 (2.50 mmol, 50% in H_2O , 0.17 mL), in this order. The resulting reaction mixtures were vigorously stirred in thermostatted (50 $^{\circ}\text{C}$) Pyrex cylindrical vessels for 5 h at atmospheric air pressure. The product analysis was performed as follows: a sample was taken from the reaction mixture, treated with an excess of solid PPh_3 (for prior reduction^[17] of cycloalkyl hydroperoxides that are the main primary products) and then analyzed by GC by using a Fisons Instruments GC 8000 series gas chromatograph with a DB-624 (J&W) capillary column and the Jasco-Borwin v.1.50 software, revealing the formation of the following mixtures: cyclohexanol (9.3%) + cyclohexanone (1.8%) and cyclopentanol (9.1%) + cyclopentanone (0.8%), for cyclohexane and cyclopentane oxidations, respectively. Blank experiments were performed for both cycloalkanes under similar reaction conditions, which confirmed that no oxidation products were obtained in the absence of precursor **1**. Additional catalytic experiments were performed in the presence of (i) either 5 or 10 equiv. (relative to **1**) of concentrated HNO_3 (46–92 μmol , 63% in H_2O), or (ii) radical traps CBrCl_3 , 2,6-di-*tert*-butyl-4-methylphenol (BHT) or Ph_2NH (2.50 mmol of each in a separate batch), displaying an almost complete suppression of catalytic activity of **1** (only traces of products, below 0.3% were observed).
- [17] G. B. Shul'pin, *J. Mol. Catal. A* **2002**, 189, 39, and references cited therein.
- [18] This activity has been achieved by using slightly different (relative to those described^[16]) reaction parameters, i.e., catalyst precursor **1** (3.0 mg, 5.5 μmol), cyclohexane (10.0 mmol), acetonitrile (3.80 mL) and H_2O_2 (10.0 mmol, 50% in H_2O , 0.68 mL).
- [19] EPR spectra of **1** were recorded (following a reviewer's suggestion) on solid crystalline samples or frozen aqueous solutions by using a Bruker ESP300E X-band spectrometer equipped with an ER 4111 VT variable-temperature unit. Typical patterns for Cu^{II} ($I = 3/2$) with $g = 2.22$ and $A = 130 \text{ G}$ (with poorly resolved hyperfine coupling) were observed for both solid (298 K) and solution (100 K) samples of **1**. A broad signal ($g = 2.16$) without hyperfine coupling was obtained for a solid sample at 100 K.
- [20] a) G. B. Shul'pin, J. Gradinaru, Y. N. Kozlov, *Org. Biomol. Chem.* **2003**, 1, 3611; b) G. B. Shul'pin, G. V. Nizova, Y. N. Kozlov, L. G. Cuervo, G. Suss-Fink, *Adv. Synth. Catal.* **2004**, 346, 317.
- [21] Additional blank experiments, carried out under similar reaction conditions,^[16] but in the absence of compound **1** and in the presence of a catalytic amount (10 μmol) of Na_2CO_3 or K_2CO_3 , reveal no activity in the oxidation of cyclohexane (i.e. only traces of products, below 0.2% of the total yield, have been detected). Moreover, the activity of **1** is not promoted to any extent by the addition of potassium or sodium carbonate.

Received: April 7, 2008
Published Online: July 7, 2008