

Bottom up synthesis for homo- and heterometallic 2,3-pyridinedicarboxylate coordination compounds



Krapa Shankar^a, Alexander M. Kirillov^b, Jubaraj B. Baruah^{a,*}

^a Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781 039, Assam, India

^b Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisbon, Portugal

ARTICLE INFO

Article history:

Received 27 July 2015

Accepted 8 October 2015

Available online 24 October 2015

Keywords:

Bottom up synthesis

Copper-pyridinedicarboxylates

Heterobimetallic complexes

Topology

Mixed metal oxides

ABSTRACT

The mononuclear copper complexes (Hdapt)[Cu(Hpydc)(pydc)(H₂O)]·H₂O (**1**) and (H₂aba)[Cu(pydc)₂(Haba)]₂·9H₂O (**2**) {where dapt = 2,4-diamino-6-phenyl-1,3,5-triazine, aba = 3-aminobenzylamine and H₂pydc = 2,3-pyridinedicarboxylic acid} were synthesized and fully characterized. Of these, compound **1** is a very good building block for the bottom up synthesis of the dicopper(II) derivative (Hdapt)₄[Cu₂(pydc)₄]·10H₂O (**3**), the heterometallic 2D coordination polymer {[Zn(H₂O)₄Cu(pydc)₂]·3H₂O}_n (**4**) and the 3D metal–organic framework {[Gd(H₂O)₅Cu_{1.5}(pydc)₃]·5H₂O}_n (**5**). The structures of **1–3** reveal the formation of distinct 2D (in **1** and **3**) and 3D (in **2**) H-bonded networks driven by strong hydrogen bonds between the Cu(pydc)₂-containing anions and amine cations. The underlying H-bonded (in **1–3**) and metal–organic (in **4** and **5**) networks were classified from a topological viewpoint, disclosing the following topologies: a SP 1-periodic net (4,4)(0,2) in **1**, a topologically unique net in **2**, a 3,6L17 layer in **3**, a 3,4L13 layer in **4** and an alb-3,6-P42/mmm framework in **5**. The thermal properties of **1–5** as well as the decomposition of **4** and **5** toward the synthesis of nano-dimensional mixed metal oxides were investigated.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Metal complexes and coordination polymers derived from different positional isomers of pyridinedicarboxylic acids [1–11] have provided a wide scope to explore them for various materials and biomedical applications [12–13]. Some metal pyridinedicarboxylate derivatives show high sensitivity in recognition of cations [14–15] and reversible water absorption [16]. The 2,3- and 2,6-pyridinedicarboxylic acids also generate special interest in crystal engineering research due to their ability to form a variety of self-assembled supramolecular and metal–organic networks [17–30]. For example, 2,6-pyridinedicarboxylate complexes of divalent metal ions generate layered structures guided by π -stacking interactions [31–32]. On the other hand, the 2,3-pyridinedicarboxylate ligand forms a mononuclear complex, shown as **A** in Chart 1, which can be considered as a dicarboxylic acid that may self-associate or interact with hydrogen acceptors such as amines to give supramolecular assemblies. Alternatively, the coordination environment of such bis-chelate compounds may expand by introduc-

ing an aqua ligand or another moiety, as illustrated in structure **B** of Chart 1. There are various other possibilities for the formation of assemblies that can include discrete di-, tri- and multinuclear complexes or coordination polymers of diverse dimensionality (see **C** in Chart 1). It is well known that various solvent molecules and cationic species can influence the structures [33–35] of pyridinedicarboxylate complexes; a number of such 2,3-pyridinedicarboxylate systems have been reported [17–19]. Additionally, pyridinedicarboxylate compounds can stabilize water clusters [36–42] through different scaffolds formed by self-assembly. The pyridinedicarboxylate coordination polymers are conventionally prepared in a single step without much concern as to the smallest inorganic building block being involved, whereas variation of the reaction conditions can lead to different products or their mixtures, especially when attempting the synthesis of heterometallic coordination polymers. In this regard, there is a concern to develop a versatile and relatively simple procedure for the generation of heterometallic metal–organic networks. Bearing this point in mind and following our general interest [43–45] in constructing new supramolecular and metal–organic assemblies from copper(II)-pyridinedicarboxylate building blocks, we have explored herein a bottom up synthetic approach using anionic copper(II)-bis(2,3-pyridinedicarboxylate) building blocks. As the cationic part we chose 2,4-diamino-6-phenyl-1,3,5-triazine (dapt) or 3-aminoben-

* Corresponding author. Tel.: +91 361 2582311; fax: +91 361 2690762.

E-mail addresses: kirillov@ist.utl.pt (A.M. Kirillov), juba@iitg.ernet.in (J.B. Baruah).

URL: <http://www.iitg.ac.in/juba> (J.B. Baruah).

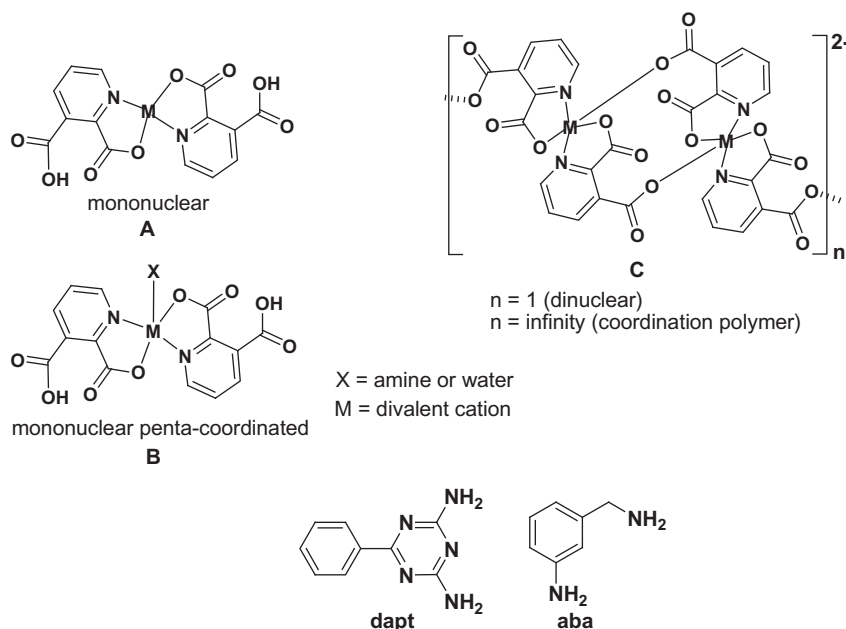


Chart 1. Schematic representation of the possible metal(II)-bis(2,3-pyridinedicarboxylate) precursors: mononuclear complex **A**, mononuclear complex with an additional ligand **B**, dinuclear complex or coordination polymer **C**. Formulae of the amines used as cationic counterparts in the present work.

zylamine (aba) as these amines possess several hydrogen bonding sites with a rigid geometry which can potentially form complementary hydrogen bonds with carboxylate ligands to give a mononuclear precursor.

Hence, in the present work, we report the synthesis of two monocopper(II) complexes, $(\text{Hdapt})[\text{Cu}(\text{Hpydc})(\text{pydc})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ (**1**) and $(\text{H}_2\text{aba})[\text{Cu}(\text{pydc})_2(\text{Haba})]_2\cdot 9\text{H}_2\text{O}$ (**2**), and the application of one of them (**1**) as a precursor for the bottom up generation of a new discrete dicopper(II) derivative, $(\text{Hdapt})_4[\text{Cu}_2(\text{pydc})_4]\cdot 10\text{H}_2\text{O}$ (**3**), as well as two novel 2D and 3D heterometallic metal–organic networks, $\text{Cu}(\text{II})/\text{Zn}(\text{II})$ $[\{\text{Zn}(\text{H}_2\text{O})_4\text{Cu}(\text{pydc})_2\}\cdot 3\text{H}_2\text{O}]_n$ (**4**) and $\text{Cu}(\text{II})/\text{Gd}(\text{III})$ $[\{\text{Gd}(\text{H}_2\text{O})_5\text{Cu}_{1.5}(\text{pydc})_3\}\cdot 5\text{H}_2\text{O}]_n$ (**5**). All the compounds **1–5** have been fully characterized and their structural and topological features are discussed in detail.

2. Experimental

2.1. General

IR spectra were recorded on a PerkinElmer Spectrum One FTIR spectrophotometer with KBr disks in the $4000\text{--}400\text{ cm}^{-1}$ range. UV–Vis spectra were recorded using a Perkin–Elmer Lambda-750 spectrometer. Thermogravimetric analysis (TGA) was performed using a Mettler Toledo instruments simultaneous DTA/TGA system, under nitrogen with a heating rate of $5\text{ }^\circ\text{C}/\text{min}$. ESR spectra were run on a JEOL, Model: JES-FA200 ESR spectrometer. Powder X-ray diffraction patterns were collected on a Bruker D2 Phaser desktop diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418\text{ \AA}$). TEM images of the oxides were taken using a JEOL, Model: JEM 2100 instrument, whereas FESEM images were taken on a Zeiss instrument.

2.2. Synthesis and characterization

Compounds **1** and **2** were prepared by a typical procedure as follows: To a solution of 2,3-pyridinedicarboxylic acid (0.167 g, 1.0 mmol) dissolved in methanol (20 mL), copper(II) acetate monohydrate (0.10 g, 0.5 mmol) was added, causing the formation

of blue precipitate. The mixture was stirred further and the corresponding amine (0.5 mmol; dapt for **1** or aba for **2**) was added in small portions. The obtained homogeneous solution was left overnight at room temperature. This resulted in the formation of blue precipitate, which was collected by filtration and dissolved in water or a water/pyridine mixture. Slow evaporation of this mixture in air yielded crystals of **1** and **2** in 3–4 days.

$(\text{Hdapt})[\text{Cu}(\text{Hpydc})(\text{pydc})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ (**1**). Isolated yield: 60%. IR (KBr, cm^{-1}): 3357 (br, s), 3084 (w), 1910 (w), 1713 (s), 1653 (s), 1609 (w), 1484 (w), 1391 (s), 1349 (s), 1271 (s), 1174 (w), 1130 (m), 1034 (m), 972 (w), 835 (m), 758 (m). UV–Vis (solid state) λ_{max} (nm): 624. ESR (solid state) g: 2.075. TGA ($^\circ\text{C}$): 40–150 ($-\text{2H}_2\text{O}$; exptl. wt. loss 5.3%, calcd. 5.9%), 150–380 (formation of CuO ; exptl. wt. loss 88.7%, calcd. 87.1%).

$(\text{H}_2\text{aba})[\text{Cu}(\text{pydc})_2(\text{Haba})]_2\cdot 9\text{H}_2\text{O}$ (**2**). Isolated yield: 29%. IR (KBr, cm^{-1}): 3452 (br), 3329 (w), 3253 (w), 1644 (s), 1586 (s), 1473 (w), 1386 (s), 1349 (s), 1275 (m), 1234 (w), 1150 (w), 1112 (s), 915 (w), 877 (m), 840 (m), 787 (w), 7287 (w), 695 (s). UV–Vis (solid state) λ_{max} (nm): 636. ESR (solid state) g: 2.075. TGA ($^\circ\text{C}$): 40–200 ($-\text{9H}_2\text{O}$; exptl. wt. loss 10.9%, calcd. 12.4%), 220–380 (formation of CuO ; exptl. wt. loss 89.1%, calcd. 88.0%).

$(\text{Hdapt})_4[\text{Cu}_2(\text{pydc})_4]\cdot 10\text{H}_2\text{O}$ (**3**). To a solution of **1** (0.309 g, 0.5 mmol) dissolved in a methanol/water mixture (1:1, 30 mL), pyridine was added (5 mmol, 0.4 mL) to maintain a pH value of 8.0; the obtained solution was refluxed for 2 h and filtered. Slow evaporation of the filtrate led to the formation of X-ray quality crystals after 4–5 days. Isolated yield 68%. IR (KBr, cm^{-1}): 3472 (bs), 3379 (bs), 2932 (w), 1628 (s), 1584 (s), 1433 (w), 1387 (w), 1366 (s), 1269 (m), 1152 (w), 1115 (m), 1022 (m), 879 (w), 832 (w), 698 (m), 605 (m). UV–Vis (solid state) λ_{max} (nm): 636. ESR (solid state) g: 2.051. TGA ($^\circ\text{C}$): 50–200 ($-\text{5H}_2\text{O}$ and $-\text{dapt}$; exptl. wt. loss 32.5%, calcd. 30.0%), 225–380 (formation of CuO ; exptl. wt. loss 89.1%, calcd. 88.0%).

$\{\text{Zn}(\text{H}_2\text{O})_4\text{Cu}(\text{pydc})_2\}\cdot 3\text{H}_2\text{O}$ (**4**). To a solution of **1** (0.309 g, 0.50 mmol) dissolved in a methanol/water mixture (1:1, 30 mL), zinc(II) acetate dihydrate (0.072 g, 0.25 mmol) was added, resulting in the formation of a blue precipitate. To the resulting reaction mixture 4–5 drops of pyridine were added to make a homogenous

Download English Version:

<https://daneshyari.com/en/article/7765004>

Download Persian Version:

<https://daneshyari.com/article/7765004>

[Daneshyari.com](https://daneshyari.com)