ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

Inorganica Chimica Acta 361 (2008) 1728–1737

Inorganica Chimica Acta

www.elsevier.com/locate/ica

3D hydrogen bonded metal-organic frameworks constructed from $[M(H_2O)_6][M'(dipicolinate)_2] \cdot mH_2O$ (M/M′ = Zn/Ni or Ni/Ni). Identification of intercalated acyclic $(H_2O)_6/(H_2O)_{10}$ clusters

Marina V. Kirillova, Alexander M. Kirillov, M. Fátima C. Guedes da Silva, Maximilian N. Kopylovich, João J.R. Fraústo da Silva, Armando J.L. Pombeiro *

Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1049–001, Lisbon, Portugal

Received 31 October 2006; accepted 3 December 2006
Available online 16 December 2006

Dedicated to Prof. Piero Zanello on the occasion of his 65th anniversary and in recognition for his contributions to inorganic electrochemistry.

Abstract

New heterodinuclear Zn^{II}/Ni^{II} (**1**) and homodinuclear Ni^{II}/Ni^{II} (**2**) water-soluble and air stable compounds of general formula $[M(H_2O)_6][M'(dipic)_2] \cdot mH_2O$ have been easily prepared by self-assembly of the corresponding metal(II) nitrates with dipicolinic acid (H_2dipic) in water solution at room temperature. The compounds have been characterized by IR, UV/Vis and atomic absorption spectroscopies, elemental and X-ray single crystal diffraction (for $\mathbf{1} \cdot 4H_2O$ and $\mathbf{2} \cdot 5H_2O$) analyses. 3D infinite polymeric networks are formed via extensive hydrogen bonding interactions involving all coordinated and crystallization water molecules, and all dipicolinate oxygens, thus contributing to additional stabilization of dimeric units, metal-organic chains and 2D layers. In $\mathbf{1} \cdot 4H_2O$, the latter represent a rectangular-grid 2D framework with multiple channels if viewed along the *c* crystallographic axis, while in $\mathbf{2} \cdot 5H_2O$ intercalated crystallization water molecules are associated to form acyclic nonplanar hexameric water clusters and water dimers which occupy voids in the host metal-organic matrix, with a structure stabilizing effect via host–guest interactions. The hexameric cluster extends to the larger $(H_2O)_{10}$ one with an unusual geometry (acyclic helical octamer with two pendent water molecules) by taking into account the hydrogen bonds to water ligands in $[Ni(H_2O)_6]^{2+}$. The obtained Zn/Ni compound **1** relates to the recently reported family of heterodimetallic complexes $[M(H_2O)_5M'(dipic)_2] \cdot mH_2O$ (M/M′ = Cu/Co, Cu/Ni, Cu/Zn, Zn/Co, Ni/Co, $m = 2, 3$), what now allows to establish the orders of the metal affinity towards the formation of chelates with dipicolinic acid ($Co^{II} > Ni^{II} > Zn^{II} > Cu^{II}$) or aqua species ($Co^{II} < Ni^{II} < Zn^{II} < Cu^{II}$).

Keywords: Crystal engineering; Dipicolinic acid; Heterometallic complexes; Hydrogen bonds; Metal-organic frameworks; Water clusters

1. Introduction

Multidimensional metal-organic frameworks constructed by means of hydrogen bonds constitute a recent class of compounds with high current interest in various areas, e.g. in supramolecular and host–guest chemistry, material science, crystal engineering, catalysis, molecular magnetism, etc. [1–11]. A considerable part of such metal-organic frameworks is based on functional components constructed from different aromatic mono- and polycarboxylic acids, which are able to generate robust and flexible H-bonding networks via extensive O–H···O interactions. In particular, pyridine-2,6-dicarboxylic acid (dipicolinic acid, H_2dipic) has been a recognized structural component in many metal-organic frameworks [12–19] not only because of the versatility of its coordination modes and affinity to form strong hydrogen bonds, but also due to the growing significance of dipicolinate containing compounds as various functional materials, in biochemistry

---

* Corresponding author. Fax: +351 21 846 4455.
E-mail address: pombeiro@ist.utl.pt (A.J.L. Pombeiro).

0020-1693/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2006.12.016

and in the formation of water clusters [20–26]. The identification and characterization of the latter in various crystalline materials has become a popular research field in recent years [27–40], thus contributing to the important understanding of the properties of bulk water in its both liquid and solid states, and water–water interactions in various environments.

In pursuit of our interest on the self-assembly synthesis and catalytic application of various polynuclear metal complexes [41–44], we have recently applied dipicolinic acid for the preparation of 3D hydrogen bonded heteronuclear Co, Ni, Cu and Zn *aqua* dipicolinate compounds [12]. Another study [45] shows that infinite chains of decameric *water clusters* can be trapped within a Cu/Na metal-organic polycarboxylate framework. As a continuation and possible combination of these studies, the current work aimed to obtain, by a simple route, new aqua dipicolinate complexes and check if their hydrogen-bonded frameworks, with a high affinity for water, could host water clusters with a mutual stabilization effect.

Hence, we report herein the easy self-assembly synthesis and full characterization of two new hexaaqua dipicolinate complexes of the type $[M(H_2O)_6][M'(dipic)_2] \cdot mH_2O$ (M/M′ = Zn^{II}/Ni^{II} or Ni^{II}/Ni^{II}), which form 3D hydrogen bonded metal-organic frameworks in the solid state. One of them was found to host water dimers and acyclic water hexamers, the latter further extending to larger $(H_2O)_{10}$ clusters with an unusual geometry (acyclic helical octamer with two pendent water molecules) via additional interactions with the $[Ni(H_2O)_6]^{2+}$ moieties.

2. Experimental

2.1. General materials and procedures

All synthetic work was performed in air and at room temperature. The water was distilled and deionized. $Ni(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, 2,6-pyridinedicarboxylic acid, nitric acid and sodium hydroxide were obtained either from Aldrich or Fluka and used as received. C, H and N elemental analyses, and atomic absorption spectroscopy analyses on metals were carried out by the Microanalytical Service of the Instituto Superior Técnico. Melting points were determined on a Kofler table. Infrared spectra (4000–400 cm^{-1}) were recorded on a Jasco FT/IR–430 instrument in KBr pellets. UV–visible spectra were recorded on a Jasco model 7800 UV/Vis spectrophotometer in water solutions.

2.2. Synthesis of $[Zn(H_2O)_6][Ni(dipic)_2] \cdot 3H_2O$ ($\mathbf{1} \cdot 3H_2O$)

To an aqueous solution (10.0 mL) containing an equimolar mixture of $Ni(NO_3)_2 \cdot 6H_2O$ (5.0 mL, 0.50 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (5.0 mL, 0.50 mmol) in HNO_3 (1.0 mmol) [the acid was added to avoid a spontaneous hydrolysis of the metal salts] were added 2,6-pyridinedicarboxylic acid (167 mg, 1.00 mmol) and dropwise an aqueous solution (2.0 mL) of NaOH (80 mg, 2.0 mmol) with continuous stirring at room temperature. The resulting mixture was stirred for 3 h, filtered off and then left to evaporate in a beaker in air at ambient temperature. Air-stable, water-soluble, greenish-blue crystals were formed within several days, then collected and dried in air to give $\mathbf{1} \cdot 3H_2O$ in ca. 50% yield based on metal nitrates. *Anal.* Calc. for $C_{14}H_{24}N_2NiO_{17}Zn$ (614.4): C, 27.28; H, 3.92; N, 4.54. Found: C, 27.57; H, 3.65; N, 4.56%. UV/Vis (H_2O): no band of $[Ni(H_2O)_6]^{2+}$. IR (KBr): 3380 (s) and 3254 (s, br) $\nu(H_2O)$, 1669 (m) $\delta(H_2O)$, 1612 (s) and 1581 (s, br) $\nu_{as}(COO)$, 1460 (m), 1428 (m), 1398 (s) and 1288 (s) $\nu_s(COO)$ cm^{-1}.

2.3. Synthesis of $[Ni(H_2O)_6][Ni(dipic)_2] \cdot 3H_2O$ ($\mathbf{2} \cdot 3H_2O$)

This compound was prepared by following the general procedure described for **1**, but using nickel(II) nitrate hexahydrate as the only metal salt (1.00 mmol in 10.0 mL of water solution). Green crystals were obtained in ca. 55% yield. *Anal.* Calc. for $C_{14}H_{24}N_2Ni_2O_{17}$ (609.7): C, 27.58; H, 3.97; N, 4.59. Found: C, 27.25; H, 4.15; N, 4.48%. UV/Vis (H_2O): $\lambda_{max} = 395$ nm $[Ni(H_2O)_6]^{2+}$. IR (KBr): 3481 (s) and 3220 (s, br) $\nu(H_2O)$, 1652 (m) $\delta(H_2O)$, 1612 (s) and 1577 (s, br) $\nu_{as}(COO)$, 1433 (m), 1385 (s) and 1286 (m) $\nu_s(COO)$ cm^{-1}.

2.4. X-ray crystal structure determinations

X-ray quality crystals of $\mathbf{1} \cdot 4H_2O$ and $\mathbf{2} \cdot 5H_2O$ were obtained from the reaction solutions (see above), then collected in air and were not dried. X-ray data were collected on an Enraf-Nonius CAD4 diffractometer, equipped with a graphite monochromator and using Mo Kα radiation ($\lambda = 0.71069$ Å). The structures were solved by direct methods using the SHELXS-97 program [46]. An empirical absorption correction based on equivalent reflections was applied. Structures were refined with the SHELXL-97 program [46]. All hydrogens were either located from the difference Fourier map or inserted in calculated positions except for O24. The crystallographic data are summarized in Table 1 and selected bond lengths and angles in Table 2.

3. Results and discussion

3.1. Synthesis and spectroscopic characterization

The compounds **1** and **2** have been synthesized by following the recently reported procedure [12] for related heterodinuclear aqua dipicolinate complexes of the type $[M(H_2O)_5M'(dipic)_2] \cdot mH_2O$ (M/M′ = Cu/Co, Cu/Ni, Cu/Zn, Zn/Co, Ni/Co, m = 2–3). Thus, addition of dipicolinic acid to an aqueous acidic solution containing either the equimolar mixture of $Zn(NO_3)_2/Ni(NO_3)_2$ (for **1**) or nickel nitrate (for **2**) as the only metal salt, followed by the