Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polyhedron 24 (2005) 295–303

ELSEVIER

POLYHEDRON

www.elsevier.com/locate/poly

Novel inorganic–organic hybrids based on oxo-bridged $M_6(M)$ centered octahedral cage

Chong Lei [a], Jiang-Gao Mao [a,*], Yan-Qiong Sun [a], Zhen-Chao Dong [b]

[a] *State Key Laboratory for Structure Chemistry, Fujian Institute for Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, People's Republic of china*

[b] *National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan*

Received 10 August 2004; accepted 17 November 2004

Available online 8 December 2004

Abstract

Three new polyoxometalates with *N*-(phosphonomethyl)-*N*-methyl glycine ($MeN(CH_2CO_2H)(CH_2PO_3H_2)$, H_3L), namely, $Cd_9L_6(H_2O)_{12} \cdot 19H_2O$ (**1**), $\{Zn_7L_6\}\{Ni(bipy)(H_2O)_4\}_2 \cdot 16H_2O$ (**2**) (bipy = 4,4-bipyridine) and $[H_3O]\{Zn_7L_6\}$ $\{Ni(H_2O)_2(bipy)_2\}_{1.5} \cdot 12H_2O$ (**3**), have been synthesized and structurally determined.The structures of all three compounds are built from oxo-bridged $M_6(M)L_6$($M = Zn$ or Cd) centered octahedral cages.In compound **1**, the $[Cd_6(Cd)L_6]$ cages are interconnected by Cd_2O_2 dimeric units into a novel $\langle 2\ 0\ 0\rangle$ layer.Packing of such 2D layers results in cavities that are occupied by lattice water molecules.The structure of compound **2** is composed of $\{Zn_6(Zn)L_6\}^{4-}$ cluster anions and 1D cationic chains of $\{Ni(bipy)(H_2O)_4\}^{2+}$.The lattice water molecules are located in the tunnels created by the above two types of building blocks which are interlinked via hydrogen bonds.In compound **3**, the $\{Zn_6(Zn)L_6\}^{4-}$ cluster anion cages are located at the tunnels formed by the 3D cationic network of$\{Ni(bipy)_2(H_2O)_2\}^{2+}$.

Keywords: Metal phosphonates; Hydrothermal synthesis; Open frameworks; Crystal structures; Cage compounds

1. Introduction

The chemistry of metal phosphonates has been an area of interest to both inorganic and materials chemists in recent years due to their potential applications in the areas of catalysis, ion exchange, proton conductivity, intercalation chemistry, photochemistry, and materials chemistry [1]. In addition to the layered species, metal phosphonates also exhibit a variety of open framework and microporous structures [1–3]. Materials with open-framework and microporous structures are expected to find their use as hybrid composite materials in electro-optical and sensing application in the future [4–8]. However, reports on metal phosphonates with a molecular cluster unit are relatively rare [9–14]. Synthesis of multi-zinc clusters is of considerable contemporary interest, as exemplified by the potential application of the trinuclear clusters in biological systems such as phospholipase C and P1 nuclease [15]. Phosphonic acid attached with a carboxylate group can function as multidentate chelating and bridging ligand, hence we deem it can also form cluster cage compounds in addition to compounds with layered or 3D structures. Two zinc(II) cage compounds have been obtained by reactions of zinc(II) acetate with *N*-(phosphonomethyl)proline or *N*-(phosphonomethyl)-*N*-methyl glycine [16]. The structures of both zinc(II) amino-carboxylate-phosphonates are composed of a $Zn_6(Zn)(ligand)_6$ cluster anion and two hexahydrated zinc(II) cations [16]. We deem that these hexahydrated zinc(II) cations should be exchangeable by other

---

[*] Corresponding author. Tel.: +86 591 3704836; fax: +86 591 3714946.

E-mail address: mjg@ms.fjirsm.ac.cn (J.-G. Mao).

0277-5387/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2004.11.007

transition metal ions, such as Co(II) and Ni(II) ions for whom an octahedral geometry is more favored. Furthermore, it is possible for these isolated hexahydrated divalent metal ions to be interconnected into a 1D array, a 2D layer or 3D network if a suitable metal linker such as 4,4′-bipyridine (bipy) is added. Another possibility is that these isolated cluster cages may be interconnected into a 2D layer by a suitable linker. Our such research initiatives afforded three new inorganic–organic hybrids based on $M_6(M)(L)_6$($H_3L = CH_3N(CH_2CO_2H)(CH_2PO_3H_2)$) cluster cages, namely, $Cd_9L_6(H_2O)_{12} \cdot 19H_2O$ (**1**), $\{Zn_7L_6\}$ $\{Ni(bipy)(H_2O)_4\}_2 \cdot 16H_2O$ (**2**) (bipy = 4,4′-bipyridine) and $[H_3O]\{Zn_7L_6\}$ $\{Ni(H_2O)_2(bipy)_2\}_{1.5} \cdot 12H_2O$ (**3**). All three compounds belong to a new type of polyoxometalates. Herein we reported their syntheses, characterizations and crystal structures.

2. Experimental

2.1. Materials and methods

N-(phosphonomethyl)-*N*-methyl glycine (H_3L) was prepared by a Mannich type reaction according to procedures previous described [16b]. All other chemicals of reagent grade were obtained from commercial sources and used without further purification. Elemental analyses for C, H, N were performed on a Vario EL III elemental analyzer. Ni and Zn elemental analyses for compounds **2** and **3** were carried out with an ICPQ-100 spectrometer. The FT-IR spectra were recorded on a Nicolet Magna 750 FT-IR spectrometer using KBr pellets in the range of 4000–400 cm^{-1}. Thermogravimetric analysis was carried out with a TGA/SBTA851 unit at a heating rate of 15 °C/min under a nitrogen atmosphere. The XRD powder patterns were collected on a Philips X'Pert-MPD diffractometer using graphite-monochromated Cu Kα radiation in the angular range $2\theta = 5–70°$ with a step size of 0.02° and a counting time of 3 seconds per step. Magnetic susceptibility measurements were performed with a Quantum Design SQUID magnetometer at a field of 1 T over the range of 6–300 K. The diamagnetic contributions of the samples were corrected using Pascal's constants.

2.2. Synthesis of $Cd_9L_6(H_2O)_{12} \cdot 19H_2O$ (1)

Compound **1** was synthesized by reacting 1.0 mmol of $CdC1_2$ with 0.5 mmol of H_3L in 10 ml of deionized water. Then the pH value of the resultant solution was adjusted to approximately 5 by adding 20 wt% tetrabutylammonium hydroxide solution. The reaction mixture was stirred at room temperature for 24 h and then filtered. Slow diffusion of ethanol into the filtrate afforded colorless crystals of **1** in a ca. 33% yield based on Cd. The final pH value is close to 5.0. Elemental analysis for **1**, $Cd_9C_{24}H_{106}N_6O_{61}P_6$: *Anal.* Calc.: C, 10.85; H, 4.03; N, 3.17. Found: C, 10.45; H, 3.87; N, 3.43%. IR data (KBr, cm^{-1}): 3383 (br), 2924(w), 2814(w), 2175(w), 1579(s), 1452(m), 1431(m), 1406(s), 1346(m), 1317(s), 1317(m), 1288(m), 1244(w), 1186(m), 1128(s), 1061(s), 972(s), 937(m), 895(m), 854(m), 787(m), 719(m), 590(m), 546(m), 526(w), 496(m).

2.3. Synthesis of $\{Zn_7L_6\}$ $\{Ni(bipy)(H_2O)_4\}_2 \cdot 16H_2O$ (2)

Compound **2** was prepared by hydrothermal reactions. A mixture of 1.0 mmol of zinc(II) acetate, 0.5 mmol of nickel(II) acetate, 1.0 mmol of H_3L and 1.0 mmol of 4,4′-bipy in 10 ml of deionized water was heated at 130 °C for 4 days. Green crystals of **2** were obtained in a 42.5% yield based on zinc. The initial and final pH values are 4.0 and 5.5, respectively. Elemental analysis for **2**, $C_{44}H_{106}N_{10}O_{54}P_6$ Zn_7Ni_2: *Anal.* Calc.: C, 22.02; H, 4.45; N, 5.84; Zn, 19.06; Ni, 4.89. Found: C, 21.81; H, 4.23; N, 5.67; Zn, 18.3; Ni, 4.5%. IR data (KBr, cm^{-1}): 3660(m), 3438(br), 2918(w), 2818(w), 1606(s), 1535(m), 1493(w), 1466(w), 1406(s), 1331(s), 1279(m), 1223(w), 1173(s), 1119(s), 1082(s), 999(s), 985(s), 933(m), 891(s), 852(s), 818(s), 791(s), 733(m), 634(m), 588(m), 553(m), 503(w), 469(w).

2.4. Synthesis of $[H_3O]\{Zn_7L_6\}\{Ni(H_2O)_2(bipy)_2\}_{1.5} \cdot 12H_2O$ (3)

The method for the preparation of compound **3** is similar to that of compound **2** except that the molar ratio of bipy/Ni was increased to 4:1. Green crystals of **3** were isolated in a 47.0% yield based on zinc. The initial and final pH values are 4.5 and 5.0, respectively. Elemental analysis for **3**, $C_{54}H_{99}N_{12}O_{46}P_6Zn_7Ni_{1.5}$: *Anal.* Calc.: C, 27.18; H, 4.19; N, 7.05; Zn, 19.2; Ni, 3.69. Found: C, 26.43; H, 4.33; N, 6.87; Zn, 18.6; Ni, 3.4%. IR data (KBr, cm^{-1}): 3419(br), 1601(s), 1537(m), 1491(w), 1450(w), 1408(s), 1335(m), 1286(w), 1225(w), 1182(m), 1120(s), 1090(s), 1072(s), 997(s), 982(s), 935(w), 895(m), 854(m), 823(s), 793(m), 733(w), 634(s), 555(s), 515(m), 467(w).

2.5. X-ray crystallography

Intensity data of compounds **1**, **2** and **3** were collected on a Siemens Smart CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. The data sets were corrected for absorption by the SADABS program [17]. All structures were solved by the direct methods and refined by full-matrix least-squares fitting on F^2 by SHELX-97 [17]. For compound **3**, O(wh) located at a position of three-fold position is assumed to be a H_3O^+ cation, and its occupancy factor