

One-dimensional copper phosphonates containing μ -halide, μ -pyridyl *N*-oxide and phosphonate bridging ligands

Yun-Sheng Ma, Tian-Wei Wang, Yi-Zhi Li, Li-Min Zheng *

State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, School of Chemistry and Chemical Engineering,
Nanjing University, Nanjing 210093, PR China

Received 18 April 2007; received in revised form 29 May 2007; accepted 29 May 2007
Available online 9 June 2007

Abstract

This paper reports the syntheses and characterization of four copper phosphonates with chain structures based on (2-pyridyl-*N*-oxide)phosphonate, namely, $[\text{Cu}_2\text{X}_2(\text{C}_5\text{H}_4\text{NOPO}_3)_2][\text{Cu}(\text{H}_2\text{O})_6] \cdot 2\text{H}_2\text{O}$ [$\text{X} = \text{Cl}$ (1), Br (2)] and $\text{CuX}(\text{C}_5\text{H}_4\text{NOPO}_3\text{H}) \cdot \text{H}_2\text{O}$ [$\text{X} = \text{Cl}$ (3), Br (4)]. Compounds 1 and 2 are isostructural and show a chain structure where Cu(1) and Cu(2) are triply bridged by halide, oxygen donor of the pyridyl *N*-oxide and O–P–O group. The $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ serves as a charge-balancing cation and locate between the chains together with the water molecules. Compounds 3 and 4 are also isostructural. In these cases, one of the three phosphonate oxygen atoms is protonated, thus leading to a neutral chain structure which is very similar to the anionic chains in compounds 1 and 2. Magnetic studies of compounds 1–4 reveal that antiferromagnetic interactions are mediated between the copper ions.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Copper; (2-Pyridyl-*N*-oxide)phosphonate; Chain structure; Magnetic property

1. Introduction

One-dimensional copper compounds have been of interest because they provide genuine examples for testing models which could not be solved in higher dimension [1]. The strong coordination capabilities of phosphonate ligands (RPO_3^{2-}) toward metal ions often lead to the formation of metal phosphonate compounds with high dimensionalities [2]. Consequently, copper phosphonates with one-dimensional structures are rather few in number. Compound $\text{Cu}[\text{NH}(\text{CH}_2\text{PO}_3\text{H})_2]$ contains dimers of Cu_2O_2 which are interconnected via phosphonate groups to form a chain [3]. In compound $[\text{Cu}(\text{terpy})(\text{HO}_3\text{PCH}_2\text{CH}_2\text{PO}_3\text{H})] \cdot 4\text{H}_2\text{O}$, the $\{\text{CuN}_3\text{O}_2\}$ square pyramids are linked by diphosphonate ligands into an undulating chain [4]. In $[\text{Cu}\{(\text{C}_7\text{H}_5\text{N}_2)\text{CH}_2\text{N}(\text{CH}_2\text{PO}_3\text{H})_2\}]$, the $\{\text{CuO}_3\text{N}_2\}$ trigonal bipyramids are bridged by $\{\text{CPO}_3\}$ tetrahedra through corner-sharing

[5]. Compound $(\text{NH}_4)_2\text{Cu}_3(\text{hedp})_2(\text{H}_2\text{O})_4$ consists of infinite anionic copper–hedp chains with a ladder-type motif, which are charge-balanced by NH_4^+ cations. The side pieces of the ladder chains are formed by corner-sharing $\{\text{CuO}_5\}$ tetragonal pyramids and $\{\text{CPO}_3\}$ tetrahedra, whereas the rungs of the ladder are formed by the $\{\text{CuO}_4\}$ planes [6]. In both $[\text{NH}_3(\text{CH}_2)_2\text{NH}_3]_2[\text{Cu}_2(\text{hedp})_2] \cdot \text{H}_2\text{O}$ and $[\text{NH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{NH}_3]_2[\text{Cu}_2(\text{hedp})_2]$, the symmetrical $\{\text{Cu}_2(\text{hedp})_2\}$ dimers are connected by edge-shared $\{\text{CuO}_5\}$ square pyramids into infinite chains [7].

In our previous work, we have shown that discrete and layered copper phosphonates based on 2-pyridylphosphonate can be obtained under hydrothermal conditions [8]. By reacting (2-pyridyl-*N*-oxide)phosphonic acid with copper salt in aqueous solution, two types of copper phosphonates with unique chain structures are resulted. Herein we report the syntheses, characterization and magnetic properties of $[\text{Cu}_2\text{X}_2(\text{C}_5\text{H}_4\text{NOPO}_3)_2][\text{Cu}(\text{H}_2\text{O})_6] \cdot 2\text{H}_2\text{O}$ [$\text{X} = \text{Cl}$ (1), Br (2)] and $\text{CuX}(\text{C}_5\text{H}_4\text{NOPO}_3\text{H}) \cdot \text{H}_2\text{O}$ [$\text{X} = \text{Cl}$ (3), Br (4)] in which the copper atoms are triply bridged by

* Corresponding author.

E-mail address: lmzheng@netra.nju.edu.cn (L.-M. Zheng).

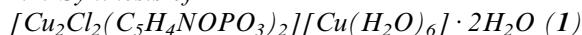
three different ligands, e.g. halide, pyridyl *N*-oxide donor and phosphonate group.

2. Experimental

2.1. Materials and methods

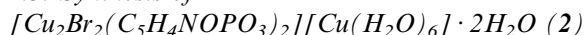
All the starting materials were reagent grade used as purchased. The (2-pyridyl-*N*-oxide)phosphonic acid (2- $C_5H_4NOPO_3H_2$) was prepared according to the literature [9]. Elemental analyses were performed on a PE 240C elemental analyzer. The infrared spectra were recorded on a VECTOR 22 spectrometer with pressed KBr pellets. Thermal analyses were performed in nitrogen with a heating rate of 10 °C/min on a Perkin–Elmer Pyris 1 TGA instrument. The magnetic susceptibility measurements were carried out on polycrystalline samples using a Quantum Design MPMS-XL7 SQUID magnetometer. The data were corrected for the diamagnetic contributions of both the sample holder and the compound obtained from Pascal's constants [10].

2.2. Synthesis of



To a solution of $Cu(O_2CCH_3)_2 \cdot H_2O$ (1 mmol, 0.20 g) in H_2O (10 mL) was added 2- $C_5H_4NOPO_3H_2$ (1 mmol, 0.175 g), the pH was adjusted to 2.00 by HCl (2 mol/L). The filtrate was evaporated for one month and pale blue crystals were collected, washed with H_2O and dried in air. Yield: 138 mg (55% based on Cu). Elemental *Anal.* Calc. for $C_{10}H_{24}Cl_2Cu_3N_2O_{16}P_2$: C, 15.98; H, 3.22; N, 3.73. Found: C, 15.92; H, 3.14; N, 3.64%. IR (KBr, cm^{-1}): 3455.6 (br), 3081.1 (br), 1624.1 (m), 1476.4 (w), 1434.0 (m), 1273.2 (w), 1197.2 (s), 1166.7 (s), 1095.7 (m), 1040.1 (s), 982.2 (s), 837.4 (s), 788.5 (m), 711.8 (m), 623.4 (m), 588.4 (w), 558.6 (m), 476.6 (w). Thermogravimetric analysis shows a two-step weight loss (18.5%) in the temperature range 50–280 °C, in agreement with the calculated value of 19.1% for the removal of eight water molecules.

2.3. Synthesis of



To a solution of $Cu(O_2CCH_3)_2 \cdot H_2O$ (1 mmol, 0.20 g) in H_2O (10 mL) was added 2- $C_5H_4NOPO_3H_2$ (1 mmol, 0.175 g), the pH was adjusted to 1.50 with HBr (2 mol/L). The filtrate was evaporated for one month and green needle-like crystals were collected, washed with H_2O and dried in air. Yield: 112 mg (40% based on Cu). Elemental *Anal.* Calc. for $C_{10}H_{24}Br_2Cu_3N_2O_{16}P_2$: C, 14.29; H, 2.88; N, 3.33. Found: C, 14.23; H, 2.86; N, 3.39%. IR (KBr, cm^{-1}): 3449.5 (br), 3095.9 (br), 1620.7 (m), 1476.3 (m), 1434.4 (m), 1272.7 (w), 1194.7 (s), 1168.5 (s), 1095.2 (m), 1034.5 (s), 978.7 (s), 835.4 (s), 785.0 (m), 712.2 (m), 623.1 (m), 586.2 (w), 557.0 (m), 477.1 (w). Thermogravi-

metric analysis shows a two-step weight loss (17.0%) in the temperature range 50–250 °C, in agreement with the calculated value of 17.1% for the removal of eight water molecules.

2.4. Synthesis of $CuCl(C_5H_4NOPO_3H) \cdot H_2O$ (3)

To a solution of $Cu(O_2CCH_3)_2 \cdot H_2O$ (1 mmol, 0.20 g) in H_2O (10 mL) was added 2- $C_5H_4NOPO_3H_2$ (1 mmol, 0.175 g), the pH was adjusted to 1.00 with HCl (2 mol/L). The filtrate was evaporated for one month and pale green crystals were collected, washed with H_2O and dried in air. Yield: 162 mg (60% based on Cu). Elemental *Anal.* Calc. for $C_5H_7ClCuNO_5P$: C, 20.63; H, 2.42; N, 4.81. Found: C, 20.68; H, 2.20; N, 4.75%. IR (KBr, cm^{-1}): 3379.4 (br), 3106.0 (m), 3078.8 (m), 1717.8 (m), 1605.3 (m), 1474.4 (m), 1427.0 (s), 1275.6 (m), 1237.5 (m), 1205.5 (m), 1154.7 (s), 1102.2 (vs), 978.7 (m), 840.8 (s), 790.6 (s), 712.7 (w), 609.2 (m), 583.9 (w), 539.3 (w), 506.6 (w), 428.5 (w). Thermogravimetric analysis shows a one-step weight loss (5.8%) in the temperature range 190–250 °C, in agreement with the calculated value of 6.2% for the removal of one water molecule.

2.5. Synthesis of $CuBr(C_5H_4NOPO_3H) \cdot H_2O$ (4)

By keeping compound **2** in the mother liquid for two months, the needle-like crystals of **2** can completely transform into block-like crystals of compound **4** with evaporation of the solvent. Yield: 119 mg (35% based on Cu). Elemental *Anal.* Calc. for $C_5H_7BrCuNO_5P$: C, 17.90; H, 2.10; N, 4.17. Found: C, 17.96; H, 1.86; N, 4.11%. IR (KBr, cm^{-1}): 3255.1(br), 3105.8 (m), 3083.4 (m), 1699.6 (m), 1604.3 (m), 1474.1 (m), 1425.9 (s), 1274.8 (m), 1239.4 (m), 1201.6 (m), 1154.7 (s), 1092.5 (vs), 979.2 (s), 838.6 (s), 787.1 (s), 712.9 (m), 609.9(s), 581.5 (m), 537.4 (w), 504.4 (m), 430.2 (w). Thermogravimetric analysis shows a one-step weight loss (5.5%) in the temperature range 190–250 °C, in agreement with the calculated value of 5.4% for the removal of one water molecule.

2.6. Crystallographic studies

Single crystals with dimensions $0.33 \times 0.27 \times 0.25 \text{ mm}^3$ for **1**, $0.25 \times 0.10 \times 0.10 \text{ mm}^3$ for **2**, $0.24 \times 0.12 \times 0.12 \text{ mm}^3$ for **3** and $0.25 \times 0.10 \times 0.10 \text{ mm}^3$ for **4** were selected for indexing and intensity data collection on a Bruker SMART APEX CCD diffractometer using graphite-monochromatized Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. A hemisphere of data were collected in the θ range 2.12–25.99° for **1**, 2.12–25.49° for **2**, 2.52–25.99° for **3** and 2.49–26.00° for **4** using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 5 s/frame. Numbers of observed and unique reflections are 6456 and 3798 ($R_{\text{int}} = 0.033$) for **1**, 8165 and 4019 ($R_{\text{int}} = 0.0351$) for **2**, 4811 and 1855 ($R_{\text{int}} = 0.038$) for **3**

Download English Version:

<https://daneshyari.com/en/article/1312719>

Download Persian Version:

<https://daneshyari.com/article/1312719>

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