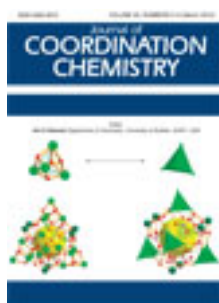


This article was downloaded by: [Renmin University of China]

On: 13 October 2013, At: 10:44

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gcoo20>

### Tube- or cage-containing layered cadmium(II) and zinc(II) phosphonates decorated by sulfone groups

Zi-Yi Du <sup>a</sup>, Cui-Cui Zhao <sup>a</sup>, Li-Jie Dong <sup>a</sup>, Xiao-Yu Deng <sup>a</sup> & Yu-Hui Sun <sup>a</sup>

<sup>a</sup> College of Chemistry and Chemical Engineering, Gannan Normal University, Ganzhou 341000, P.R. China

Published online: 21 Feb 2012.

To cite this article: Zi-Yi Du, Cui-Cui Zhao, Li-Jie Dong, Xiao-Yu Deng & Yu-Hui Sun (2012) Tube- or cage-containing layered cadmium(II) and zinc(II) phosphonates decorated by sulfone groups, Journal of Coordination Chemistry, 65:5, 813-822, DOI: [10.1080/00958972.2012.662642](http://dx.doi.org/10.1080/00958972.2012.662642)

To link to this article: <http://dx.doi.org/10.1080/00958972.2012.662642>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

## Tube- or cage-containing layered cadmium(II) and zinc(II) phosphonates decorated by sulfone groups

ZI-YI DU\*, CUI-CUI ZHAO, LI-JIE DONG,  
XIAO-YU DENG and YU-HUI SUN

College of Chemistry and Chemical Engineering,  
Gannan Normal University, Ganzhou 341000, P.R. China

(Received 29 July 2011; in final form 19 December 2011)

Hydrothermal reactions of cadmium(II) or zinc(II) ion with dimethyl methylsulfonemethane-phosphonate afforded two new layered metal phosphonates with  $\mu_2$ -H<sub>2</sub>O or  $\mu_3$ -OH<sup>-</sup> as co-ligand, [Cd<sub>2</sub>(L)<sub>2</sub>(H<sub>2</sub>O)] (**1**) and [Zn<sub>3</sub>(L)<sub>2</sub>(OH)<sub>2</sub>] (**2**) (L<sup>2-</sup> = CH<sub>3</sub>SO<sub>2</sub>CH<sub>2</sub>PO<sub>3</sub><sup>2-</sup>). The layered structure in **1** features two types of topologically similar tubes arranged in a crisscross pattern, one of which accommodates  $\mu_2$ -H<sub>2</sub>O ligands located at the tube center. The  $\mu_3$ -OH<sup>-</sup> ligands in **2** bridge the Zn<sup>2+</sup> to build a layered framework which features edge-sharing Zn<sub>6</sub>O<sub>6</sub> rings; furthermore, a pair of pentadentate L<sup>2-</sup> ligands, each binding four Zn<sup>2+</sup> ions, cap the Zn<sub>6</sub>O<sub>6</sub> ring above and below to form a Zn<sub>6</sub>P<sub>2</sub>O<sub>12</sub> cage related by 2-fold symmetry.

*Keywords:* Cadmium; Zinc; Phosphonate; Oxo-bridging; Layered structure

### 1. Introduction

Simple metal phosphonates are apt to organize molecules into lamellar structures, wherein the metal ions are bridged by phosphonates to form a dense inorganic layer and the remaining organic group of the phosphonate generally dangles in the interlayer region [1–4].

Recently, we have been interested in incorporating oxo-bridging hydroxide (H<sub>2</sub>O or OH<sup>-</sup>) as co-ligand in the inorganic layer of transition-metal phosphonates, which not only create new layered structures but also facilitate magnetic superexchange of the metal centers. Up to now, the combinations of phosphonate and oxo-bridging hydroxide in layered or pillar-layered transition-metal phosphonates have only been occasionally reported [5–15]. Our current synthetic method is directly attaching a simple sulfone to the phosphonate (i.e., CH<sub>3</sub>SO<sub>2</sub>CH<sub>2</sub>PO<sub>3</sub>H<sub>2</sub>). The sulfone usually exhibits weak coordination to metal ions but participates in hydrogen-bonding primarily with metal-bound hydroxide (H<sub>2</sub>O or/and OH<sup>-</sup>) [16]. Hence, we expect that placing a sulfone on the phosphonate may promote the presence of a metal-bound hydroxide.

By using the above ligand as a potential building block, we have obtained layered iron(III) and cobalt(II) phosphonates, [Fe(L)(OH)(H<sub>2</sub>O)] and [Co<sub>4</sub>(L)<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>] · 2H<sub>2</sub>O

\*Corresponding author. Email: ziyidu@gmail.com

( $L^{2-} = CH_3SO_2CH_2PO_3^{2-}$ ), which contain  $\mu_2-OH^-$  or  $\mu_2-H_2O$  as co-ligand, respectively [17]. Extension of the method has also afforded layered cadmium(II) and zinc(II) phosphonates with  $\mu_2-H_2O$  or  $\mu_3-OH^-$  as co-ligands,  $[Cd_2(L)_2(H_2O)]$  (**1**) and  $[Zn_3(L)_2(OH)_2]$  (**2**). So far, only a few metal complexes based on sulfone-phosphonate ligands have been reported [17, 18]. Herein, we report the syntheses, crystal structures, and thermostabilities of **1** and **2**.

## 2. Experimental

### 2.1. Materials and instrumentation

Dimethyl methylsulfonmethanephosphonate ( $CH_3SO_2CH_2PO(OCH_3)_2$ ) was synthesized using a published procedure [19]. All other chemicals were obtained from commercial sources and used without purification. Elemental analyses were performed on a German Elementary Vario EL III instrument. FT-IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer using KBr pellets from 4000 to  $400\text{ cm}^{-1}$ . X-ray powder diffraction (XRD) patterns (Cu-K $\alpha$ ) were collected on a Bruker Advance D8  $\theta$ - $2\theta$  diffractometer. Thermogravimetric analyses (TGA) were carried out on a Diamond TG/DTA 6000 unit at a heating rate of  $15^\circ\text{C min}^{-1}$  under nitrogen.

### 2.2. Synthesis of $[Cd_2(L)_2(H_2O)]$ (**1**)

A mixture of  $Cd(NO_3)_2 \cdot 4H_2O$  (0.30 mmol) and  $CH_3SO_2CH_2PO(OCH_3)_2$  (0.30 mmol) in 12 mL distilled water, with pH adjusted to about 6.0 *via* the addition of three drops of 10% NaOH solution, was sealed into a Parr Teflon-lined autoclave (23 mL) and heated at  $150^\circ\text{C}$  for 3 days. The final pH was 5.5 and colorless plate-shaped crystals of **1** were collected in 72% yield based on Cd. Anal. Calcd for  $C_4H_{12}O_{11}S_2P_2Cd_2$  ( $M_r = 587.00$ ) (%): C, 8.18; H, 2.06. Found (%): C, 8.11; H, 2.15. IR data (KBr,  $\text{cm}^{-1}$ ): 3413(s), 3042(m), 3015(m), 2984(m), 2920(m), 2403(m), 1642(m), 1565(s), 1415(m), 1330(m), 1283(s), 1202(s), 1140(vs), 1105(vs), 1071(s), 999(s), 981(s), 842(s), 787(m), 587(m), 546(m), 515(s), 461(m).

### 2.3. Synthesis of $[Zn_3(L)_2(OH)_2]$ (**2**)

A mixture of  $Zn(OAc)_2 \cdot 2H_2O$  (0.30 mmol),  $ZnCl_2$  (0.10 mmol), and  $CH_3SO_2CH_2PO(OCH_3)_2$  (0.30 mmol) in 12 mL distilled water was sealed into a Parr Teflon-lined autoclave (23 mL) and heated at  $150^\circ\text{C}$  for 3 days. The final pH was 4.0 and colorless plate-shaped crystals of **2** were collected in 81% yield based on Zn. Anal. Calcd for  $C_4H_{12}O_{12}S_2P_2Zn_3$  ( $M_r = 574.31$ ) (%): C, 8.37; H, 2.11. Found (%): C, 8.32; H, 2.29. IR data (KBr,  $\text{cm}^{-1}$ ): 3401(s), 3021(m), 2969(m), 2912(m), 2438(m), 1640(m), 1575(m), 1416(m), 1303(m), 1144(vs), 1096(vs), 1063(s), 1007(s), 965(s), 859(s), 790(s), 620(s), 588(m), 546(m), 516(s), 467(m).

Table 1. Summary of crystal data and structural refinements for **1** and **2**.

| Compound  | <b>1</b>   | <b>2</b>   |
|---|--|--|
| Empirical formula   | C <sub>4</sub> H <sub>12</sub> O <sub>11</sub> S <sub>2</sub> P <sub>2</sub> Cd <sub>2</sub> | C <sub>4</sub> H <sub>12</sub> O <sub>12</sub> S <sub>2</sub> P <sub>2</sub> Zn <sub>3</sub> |
| Formula weight  | 587.00   | 574.31   |
| Space group   | C2/c   | C2/c   |
| Unit cell dimensions (Å, °)   |  |  |
| <i>a</i>  | 24.356(3)  | 10.8522(2)   |
| <i>b</i>  | 5.2857(7)  | 5.4427(1)  |
| <i>c</i>  | 10.7212(15)  | 23.8306(5)   |
| $\alpha$  | 90   | 90   |
| $\beta$   | 94.594(9)  | 95.076(1)  |
| $\gamma$  | 90   | 90   |
| Volume (Å <sup>3</sup> ), <i>Z</i>  | 1375.8(3), 4   | 1402.04(5), 4  |
| Calculated density (g cm <sup>-3</sup> )                                    | 2.834  | 2.721  |
| Absorption coefficient (mm <sup>-1</sup> )                                  | 3.679  | 5.680  |
| Goodness-of-fit on <i>F</i> <sup>2</sup>                                    | 1.076  | 1.090  |
| <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )] | 0.0186, 0.0458   | 0.0292, 0.0797   |
| <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)                   | 0.0213, 0.0473   | 0.0330, 0.0822   |

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|; wR_2 = \{\Sigma w[(F_o)^2 - (F_c)^2]^2 / \Sigma w[(F_o)^2]^2\}^{1/2}.$$

#### 2.4. Single-crystal structure determination

Data collection for **1** and **2** were performed on a Smart ApexII CCD diffractometer equipped with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Intensity data for both compounds were collected using  $\omega$  scans at 296 K. The data sets were corrected for Lorentz and polarization factors as well as for absorption by SADABS [20]. Both structures were solved by direct methods and refined by full-matrix least-squares on *F*<sup>2</sup> by SHELX-97 [21]. C-bound hydrogen atoms were generated geometrically while O-bound hydrogen atoms were located in the difference Fourier map. All non-hydrogen atoms were refined with anisotropic thermal parameters whereas all hydrogen atoms were refined isotropically. Crystallographic data and structural refinements for **1** and **2** are summarized in table 1. Important bond lengths are listed in table 2. More details about the crystallographic data have been deposited as "Supplementary material."

### 3. Results and discussion

#### 3.1. Syntheses

The preparations of **1** and **2** rely on the well-established hydrothermal method, using dimethylphosphonate as starting material. During the course of the hydrothermal treatment, high temperature and high pressure help hydrolyze the phosphonic ester to produce phosphonic acid *in situ*. The slow formation of phosphonic acid facilitates the growth of single crystals [22, 23].

#### 3.2. Structure description for [Cd<sub>2</sub>(L)<sub>2</sub>(H<sub>2</sub>O)] (1)

Compound **1** crystallizes in the monoclinic space group C2/c and features a double-layered structure. The asymmetric unit contains one Cd<sup>2+</sup>, one L<sup>2-</sup>, and a half-occupied

Table 2. Selected bond lengths (Å) for **1** and **2**.

| <b>1</b>     |            |              |            |
|--------------|------------|--------------|------------|
| Cd(1)–O(1)   | 2.192(2)   | Cd(1)–O(3)#1 | 2.215(2)   |
| Cd(1)–O(2)#2 | 2.250(2)   | Cd(1)–O(2)#3 | 2.309(2)   |
| Cd(1)–O(5)#3 | 2.369(2)   | Cd(1)–O(1W)  | 2.449(2)   |
| S(1)–O(4)    | 1.442(2)   | S(1)–O(5)    | 1.4552(19) |
| S(1)–C(2)    | 1.741(3)   | S(1)–C(1)    | 1.762(3)   |
| P(1)–O(3)    | 1.5061(19) | P(1)–O(1)    | 1.5150(19) |
| P(1)–O(2)    | 1.5301(18) | P(1)–C(1)    | 1.832(3)   |
| <b>2</b>     |            |              |            |
| Zn(1)–O(3)#1 | 2.042(2)   | Zn(1)–O(6)   | 2.058(2)   |
| Zn(1)–O(2)   | 2.232(2)   | Zn(2)–O(6)#2 | 1.949(2)   |
| Zn(2)–O(1)#3 | 1.953(2)   | Zn(2)–O(2)   | 1.983(2)   |
| Zn(2)–O(6)#4 | 2.051(2)   | Zn(2)–O(5)   | 2.575(2)   |
| S(1)–O(4)    | 1.442(2)   | S(1)–O(5)    | 1.448(2)   |
| S(1)–C(2)    | 1.751(4)   | S(1)–C(1)    | 1.774(3)   |
| P(1)–O(3)    | 1.505(2)   | P(1)–O(1)    | 1.524(2)   |
| P(1)–O(2)    | 1.535(2)   | P(1)–C(1)    | 1.814(3)   |

Symmetry codes: For **1**: #1  $x, -y+1, z+1/2$ ; #2  $-x+1, y, -z+1/2$ ; #3  $x, -y, z+1/2$ . For **2**: #1  $x, y+1, z$ ; #2  $x+1/2, y-1/2, z$ ; #3  $x+1/2, y+1/2, z$ ; #4  $-x, y, -z+3/2$ .

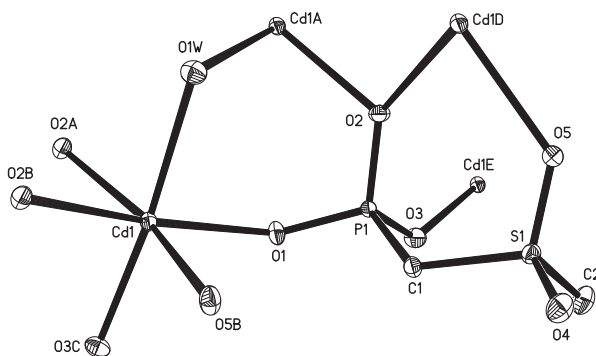


Figure 1. ORTEP representation of the selected unit of **1**. The thermal ellipsoids are drawn at 30% probability. Symmetry codes for the generated atoms: A.  $1-x, y, 1/2-z$ ; B.  $x, -y, 1/2+z$ ; C.  $x, 1-y, 1/2+z$ ; D.  $x, -y, -1/2+z$ ; E.  $x, 1-y, -1/2+z$ .

aqua ligand. Cd(1) is octahedrally coordinated by four phosphonate and one sulfone oxygen atoms from four  $L^{2-}$  anions as well as a water (figure 1). The Cd–O distances are in the range 2.1921(19)–2.4493(17) Å.

There is a pentadentate  $L^{2-}$  and  $\mu_2$ -H<sub>2</sub>O present in **1**. The  $L^{2-}$  adopts a  $[4.2_{12}1_31_41_10]$  coordination mode according to the Harris notation [24]. The ligand bridges four Cd<sup>2+</sup> ions *via* three phosphonate and one sulfone oxygen atoms, with one phosphonate functioning as  $\mu_2$ -O (figure 1). The interconnection of Cd<sup>2+</sup> by  $L^{2-}$  results in the formation of a double-layered structure, which can be viewed as cross-linkage of two types of 1-D double-chains of  $[Cd_2(L)_2]$  along the *b*- and *c*-axes, namely, chains **I** and **II**, respectively (figure 2). Chain **I** is constructed by alternating edge-sharing four-membered Cd<sub>2</sub>O<sub>2</sub> and eight-membered Cd<sub>2</sub>P<sub>2</sub>O<sub>4</sub> rings, with pairs of six-membered Cd<sub>1</sub>S<sub>1</sub>P<sub>1</sub>C<sub>1</sub>O<sub>2</sub> rings anchored on both sides of the chain. The chain is interlinked to two neighboring chains **I** by pairs of unidentate O(1) above and below the Cd<sub>2</sub>P<sub>2</sub>O<sub>4</sub> rings,

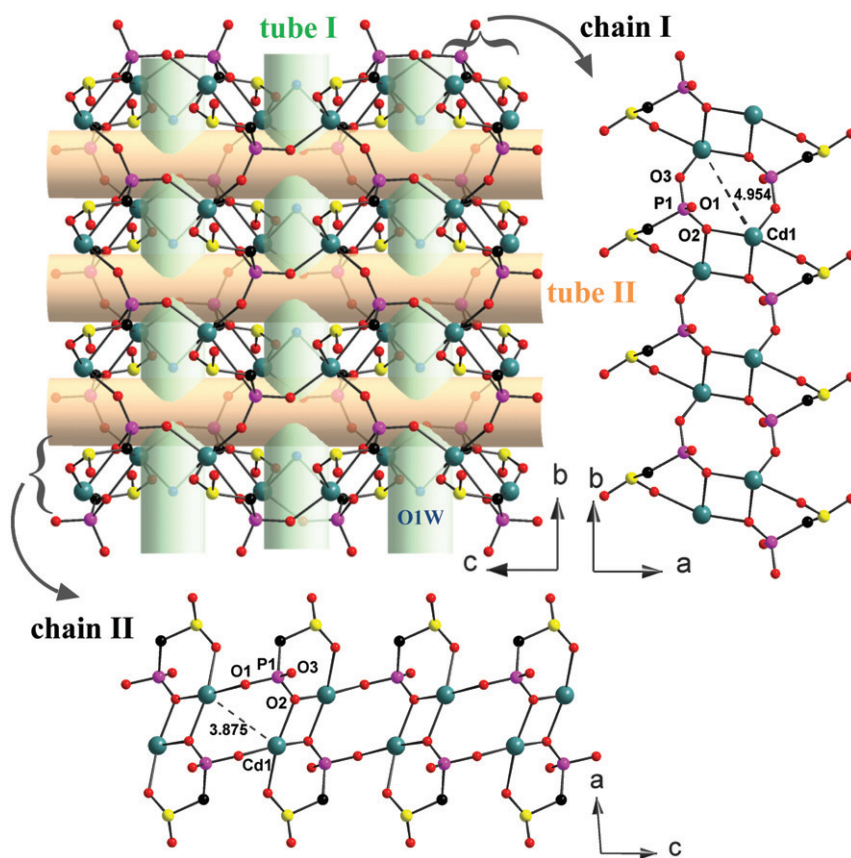


Figure 2. View of double-layered structure of **1** down the  $a$ -axis. The terminal methyl groups of  $L^{2-}$  ligands have been omitted for clarity. Cd, P, S, and C are represented by teal, purple, yellow, and black circles, respectively. Oxygen atoms from  $L^{2-}$  ligand and water molecules are represented by red and blue circles, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

leaving an open-ended tube **I** extending along the  $b$ -axis with a crystallographically imposed 2-fold axis running through the tube center. Chain **II** is a conformational isomer of Chain **I**, although the  $\text{Cd}\cdots\text{Cd}$  distances in the  $\text{Cd}_2\text{P}_2\text{O}_4$  rings are very different (4.9541(5) and 3.8751(5) Å, respectively). Correspondingly, the interlinkage of two adjacent chains **II** results in the formation of tube **II**, which is topologically similar to tube **I**. Tubes **I** and **II** are arranged in a crisscross pattern. One distinct difference is that tube **I** accommodates  $\mu_2\text{-H}_2\text{O}$  ligands located at the tube center, while tube **II** does not contain water. We note that the layers in **1** are assembled into a 3-D structure *via* van der Waals forces and there exists no lattice water in the whole structure (figure 3).

### 3.3. Structure description for $[\text{Zn}_3(\text{L})_2(\text{OH})_2]$ (**2**)

Compound **2** also crystallizes in the monoclinic space group  $C2/c$  but features another type of layered structure. The asymmetric unit contains one and one half-occupied

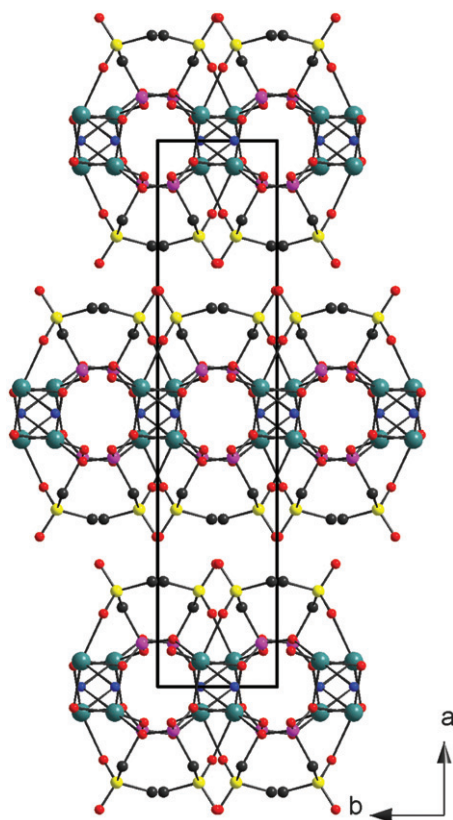


Figure 3. View of the structure of **1** down the *c*-axis. (For display details, see the caption for Figure 2).

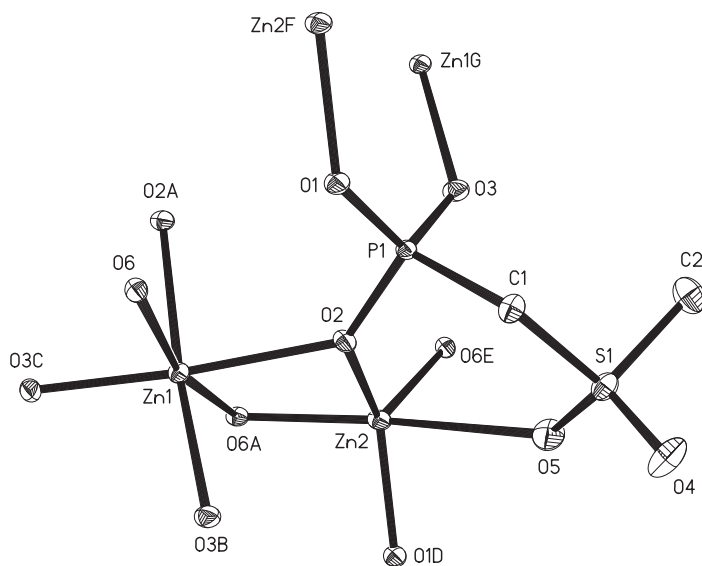


Figure 4. ORTEP representation of the selected unit of **2**. The thermal ellipsoids are drawn at 30% probability. Symmetry codes for the generated atoms: A.  $-x, y, 3/2 - z$ ; B.  $x, 1 + y, z$ ; C.  $-x, 1 + y, 3/2 - z$ ; D.  $1/2 + x, 1/2 + y, z$ ; E.  $1/2 + x, -1/2 + y, z$ ; F.  $-1/2 + x, -1/2 + y, z$ ; G.  $x, -1 + y, z$ .

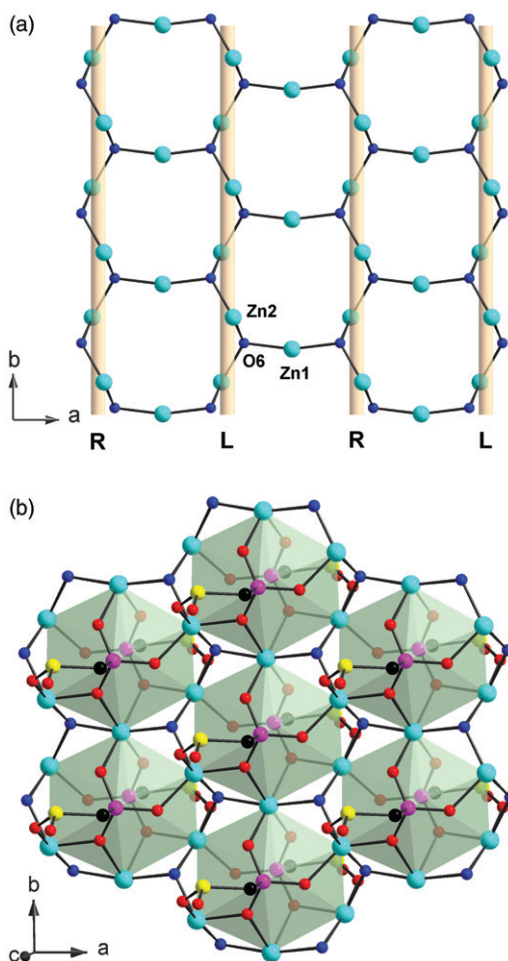


Figure 5. (a) The interconnection of Zn<sup>2+</sup> ions by the μ<sub>3</sub>-OH<sup>-</sup> ligands in **1**. (b) View of the layered structure of **1** down the *c*-axis. The terminal methyl groups of L<sup>2-</sup> ligands have been omitted for clarity. Zn, P, S, and C are represented by cyan, purple, yellow, and black circles, respectively. Oxygen atoms from the L<sup>2-</sup> ligands and the hydroxyl anions are represented by red and blue circles, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Zn<sup>2+</sup>, one L<sup>2-</sup>, and one OH<sup>-</sup>. While Zn(1) lying on a 2-fold axis is octahedrally coordinated by two OH<sup>-</sup> and four phosphonate oxygen atoms of four L<sup>2-</sup>, Zn(2) is located at a general position and is five-coordinate by two OH<sup>-</sup> anions, two phosphonates, and one weakly coordinated sulfone oxygen atom of two L<sup>2-</sup> (figure 4). The Zn–O bond distances [1.949(2)–2.232(2) Å] are normal, with the exception of one longer Zn–O distance [2.575(2) Å].

A pentadentate L<sup>2-</sup> and a μ<sub>3</sub>-OH<sup>-</sup> exist in **2**. L<sup>2-</sup> exhibits the same coordination mode as in **1**. The μ<sub>3</sub>-OH<sup>-</sup> ligands bridge Zn<sup>2+</sup> ions to build a 2-D layered framework, which can also be viewed as alternately arranged left- and right-handed helical [Zn(2)O] chains interconnected by Zn(1) ions (figure 5a). The layered framework features a 12-membered Zn<sub>6</sub>O<sub>6</sub> ring unit, which is edge-sharing with six neighboring rings. Furthermore, a pair of the pentadentate L<sup>2-</sup> ligands, each binding four Zn<sup>2+</sup> ions, cap



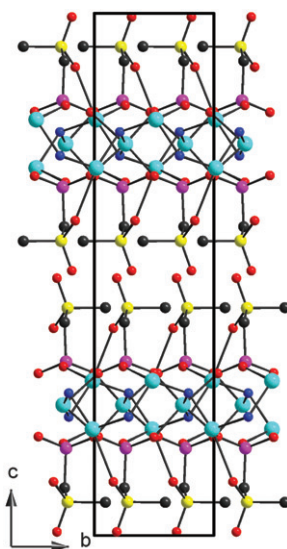


Figure 6. View of the structure of **2** down the *a*-axis. (For display details, see the caption for Figure 5).

the  $\text{Zn}_6\text{O}_6$  ring above and below to form a  $\text{Zn}_6\text{P}_2\text{O}_{12}$  cage related by 2-fold symmetry (figure 5b). In the cage, the three diagonal  $\text{Zn}\cdots\text{Zn}$  distances of the  $\text{Zn}_6\text{O}_6$  ring are 5.4427(6), 6.0703(5), and 6.0703(5) Å, respectively, while the  $\text{P}\cdots\text{P}$  distance of the two capped phosphonate groups is 3.927(1) Å. Although similar  $\text{Zn}_6\text{O}_6$  rings have been observed in discrete cluster compounds [25–28], a  $\text{Zn}_6\text{O}_6$  ring capped by a phosphonate has not been reported. The layers in **2** are also assembled into a 3-D structure *via* van der Waals forces and there are no lattice water molecules in the whole structure (figure 6).

### 3.4. TGA studies

The TGA curve of **1** exhibits three main steps of weight loss (figure 7). The first begins at 240°C and is completed at 347°C, which corresponds to release of one water molecule. The observed weight loss of 3.4% is similar to the calculated value (3.1%). The second and the third steps are overlapping and begin at 392°C and complete at 586°C, which correspond to the decomposition of the sulfone-phosphonate ligand. The total weight loss at 700°C is 32.3% and the final residuals have not been characterized. The TGA curve of **2** shows one step of sharp weight loss, which begins at 370°C and is completed at 456°C, corresponding to the decomposition of the ligands. The total weight loss at 700°C is 33.0% and the final residuals have not been characterized.

## 4. Conclusions

Hydrothermal syntheses, crystal structures, and thermostabilities of two new layered cadmium(II) or zinc(II) phosphonates based on a simple sulfone-phosphonate ligand,

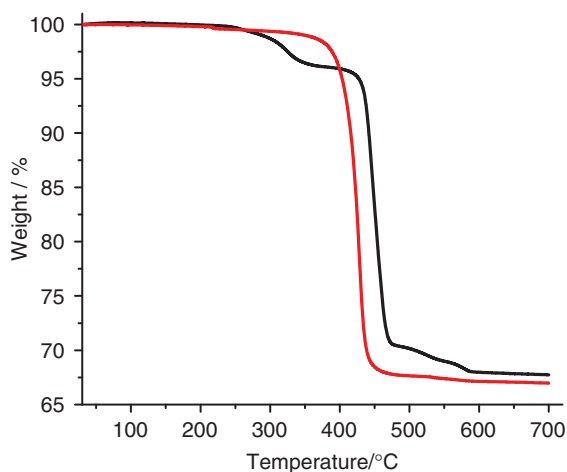


Figure 7. TGA curves for **1** (black) and **2** (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

$[\text{Cd}_2(\text{L})_2(\text{H}_2\text{O})]$  (**1**) and  $[\text{Zn}_3(\text{L})_2(\text{OH})_2]$  (**2**) ( $\text{L}^{2-} = \text{CH}_3\text{SO}_2\text{CH}_2\text{PO}_3^{2-}$ ), have been described. Although the layered structures of the two compounds are very different to those of previously reported iron(III) and cobalt(II) phosphonates based on the same sulfone-phosphonate ligand [17], the hydroxides function as bridging ligands. The results of our studies indicate that the attachment of a hydrophilic sulfone to the phosphonate can promote the presence of a bridging hydroxide co-ligand, which may be a new synthetic route for creating transition-metal phosphonates with new layered structures. Further research will be extended to use such method for the syntheses of non-transition metal phosphonates that feature novel layered structures.

### Supplementary material

CCDC 832878 and 832879 contain the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223336033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

### Acknowledgments

The work was supported by the National Natural Science Foundation of China (No. 21061001) and the Natural Science Foundation of Jiangxi Provincial Education Department (No. GJJ10714).

## References

- [1] G. Cao, H.-G. Hong, T.E. Mallouk. *Acc. Chem. Res.*, **25**, 420 (1992).
- [2] A. Clearfield. In *Progress in Inorganic Chemistry*, K.D. Karlin (Ed.), Vol. 47, p. 371, Wiley, New York (1998).
- [3] K. Maeda. *Microporous Mesoporous Mater.*, **73**, 47 (2004).
- [4] G.K.H. Shimizu, R. Vaidhyanathan, J.M. Taylor. *Chem. Soc. Rev.*, **38**, 1430 (2009).
- [5] M.I. Khan, Y.-S. Lee, C.J. O'Connor, R.C. Haushalter, J. Zubieta. *J. Am. Chem. Soc.*, **116**, 4525 (1994).
- [6] S. Drumel, P. Janvier, M. Bujoli-Doeuff, B. Bujoli. *Inorg. Chem.*, **35**, 5786 (1996).
- [7] A. Distler, F.L. Lohse, S.C. Sevov. *J. Chem. Soc., Dalton Trans.*, 1805 (1999).
- [8] N. Guillou, Q. Gao, M. Nogue, A.K. Cheetham, G. Ferey. *Solid State Sci.*, **4**, 1179 (2002).
- [9] Z.-M. Sun, J.-G. Mao, Z.-C. Dong. *Polyhedron*, **24**, 571 (2005).
- [10] J.-J. Hou, X.-M. Zhang. *Cryst. Growth Des.*, **6**, 1445 (2006).
- [11] Y.-S. Ma, Y. Song, W.-X. Du, Y.-Z. Li, L.-M. Zheng. *Dalton Trans.*, 3228 (2006).
- [12] A. Sonnauer, N. Stock. *Eur. J. Inorg. Chem.*, 5038 (2008).
- [13] A. Sonnauer, M. Feyand, N. Stock. *Cryst. Growth Des.*, **9**, 586 (2009).
- [14] J. Jokiniemi, J.J. Vepsäläinen, H. Natkinniemi, S. Peraniemi, M. Ahlgren. *CrystEngComm*, **11**, 2431 (2009).
- [15] P. DeBurgomaster, H. Liu, W. Ouellette, C.J. O'Connor, J. Zubieta. *Inorg. Chim. Acta*, **363**, 4065 (2010).
- [16] N. Furukawa, H. Fujihara. In *The Chemistry of Sulphones and Sulphoxides*, S. Patai, Z. Rappoport, C. Stirling (Eds), pp. 541–582, Wiley & Sons, New York (1988).
- [17] Z.-Y. Du, H.-R. Wen, C.-M. Liu, Y.-H. Sun, Y.-B. Lu, Y.-R. Xie. *Cryst. Growth Des.*, **10**, 3721 (2010).
- [18] Z.-Y. Du, Y.-H. Sun, X. Xu, G.-H. Xu, Y.-R. Xie. *Eur. J. Inorg. Chem.*, 4865 (2010).
- [19] I. Shahak, J. Almog. *Synthesis*, 170 (1969).
- [20] APEX2, SADABS and SAINT, Bruker AXS Inc., Madison, Wisconsin, USA (2008).
- [21] G.M. Sheldrick. *SHELX-96 Program for Crystal Structure Determination*, University of Göttingen, Germany (1996).
- [22] G.B. Hix, B.M. Kariuki, M. Tremayne. *Inorg. Chem.*, **40**, 1477 (2001).
- [23] X.-M. Zhang. *Coord. Chem. Rev.*, **249**, 1201 (2005).
- [24] R.A. Coxall, S.G. Harris, D.K. Henderson, S. Parsons, P.A. Tasker, R.E.P. Winpenny. *Dalton Trans.*, 2349 (2000).
- [25] M.B. Dinger, M.J. Scott. *Inorg. Chem.*, **40**, 1029 (2001).
- [26] S.R. Boss, R. Haigh, D.J. Linton, P. Schooler, G.P. Shields, A.E.H. Wheatley. *Dalton Trans.*, 1001 (2003).
- [27] A.B.S. Curtiss, M. Bera, G.T. Musie, D.R. Powell. *Dalton Trans.*, 2717 (2008).
- [28] A. Arbaoui, C. Redshaw, M.R.J. Elsegood, V.E. Wright, A. Yoshizawa, T. Yamato. *Adv. Inorg. Biochem.*, **5**, 621 (2010).