



## Two new layer structures of zinc(II) or strontium(II) diphosphonates based on N,N-dimethylaminomethane-1,1-diphosphonate ligand

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### ABSTRACT

Hydrothermal reactions of  $Zn^{2+}$  or  $Sr^{2+}$  ion with N,N-dimethylaminomethane-1,1-diphosphonic acid ( $H_4L$ ) afforded two new layered metal diphosphonates, namely,  $[Zn_2(H_2L)_2] \cdot 2H_2O$  (**1**) and  $[Sr_3(H_2L)_2(H_3L)_2(H_2O)_2] \cdot 2H_2O$  (**2**). The layer structure in **1** features a square-grid unit with  $Zn1O_6$  octahedra acting as nodes, which tetradentately traps one  $Zn2$  ion inside it. On the other hand, the layer architecture of **2** exhibits an unusual corner-sharing  $Sr_3O_{17}$  tri-polyhedra unit; and such trimer unit is edge-shared with two neighboring trimers, which further chelate a third trimer to form a square-grid ring with two aqua molecules residing in it. The diphosphonate ligand in the two compounds manifests diversified coordination modes accompanying with a cooperative coordination effect of its two closely linked phosphonate moieties.

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### 1. Introduction

During the past few decades, the syntheses of metal phosphonates with various structures has attracted much attention, owing to their potential applications in areas of catalysis, ion exchange, proton conductivity, intercalation chemistry, photochemistry, and material chemistry [1].

Among many of the mono- or diphosphonate ligands studied so far, methylenediphosphonic acid and its derivatives are quite unique because they feature a close connection of two phosphonate moieties via one carbon atom, which facilitate their cooperative coordination ability of acting as a  $[CP_2O_6]$  unit rather than two  $[CPO_3]$  units. As a result, they could show diversified coordination capabilities with metal ions and thus lead to the formation of new structural types [2–6].

Recently, by using such type of ligand, i.e. N,N-dimethylaminomethane-1,1-diphosphonic acid ( $H_4L$ ), we have isolated a series of metal diphosphonates such as  $Al^{3+}$ ,  $Fe^{3+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$  and  $Ba^{2+}$ , which exhibit variable structures such as 0D, 1D, double-1D, double-2D, and 3D structures [7]. Additionally, the solution complexation of some trivalent metal ions and uranyl ion ( $In^{3+}$ ,  $Ga^{3+}$ ,  $Fe^{3+}$ ,  $Ga^{3+}$ ,  $Nd^{3+}$ ,  $UO_2^{2+}$ ) with  $H_4L$  had been examined by Bollinger and Roundhill [8]. Our studies indicated that such ligand can show various coordination modes accompanying with a cooperative coordination effect of its two closely linked phosphonate moieties (Scheme 1). Also, it was found that such cooperative coordination ability may be influenced by the coordination property of a specific

metal ion (i.e., ionic radius, coordination geometry, and coordination number, etc.). As an expansion of our previous work, we have also obtained two new layered metal diphosphonates, namely,  $[Zn_2(H_2L)_2] \cdot 2H_2O$  (**1**) and  $[Sr_3(H_2L)_2(H_3L)_2(H_2O)_2] \cdot 2H_2O$  (**2**). The diphosphonate ligand in the two compounds manifests diversified coordination modes, most of which have not been reported previously. Herein, we report their syntheses, crystal structures and characterizations.

### 2. Experimental

#### 2.1. Materials and methods

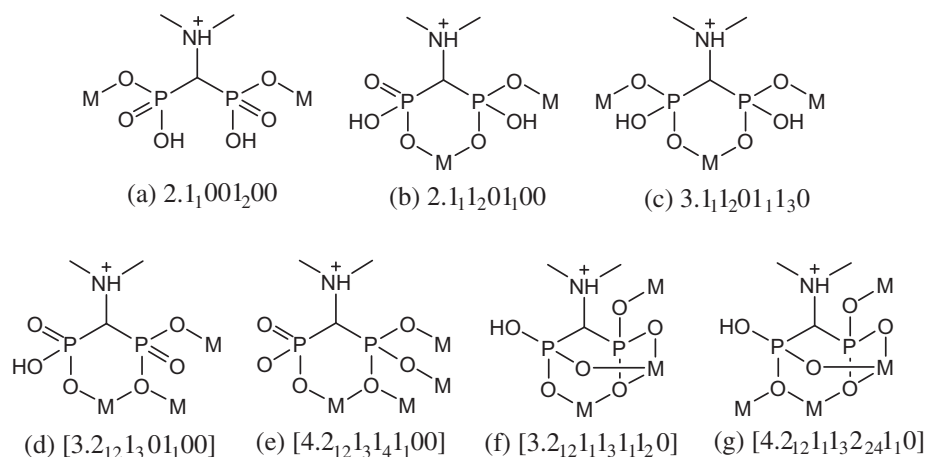
N,N-dimethylaminomethane-1,1-diphosphonic acid was synthesized using a published procedure [8a]. All other chemicals were obtained from commercial sources and used without further purification. Elemental analyses were performed on a German Elementary Vario EL III instrument. FT-IR spectra were recorded on a Perkin–Elmer Spectrum 2000 FT-IR spectrometer using KBr pellets in the range of  $4000\text{--}400\text{ cm}^{-1}$ . Thermogravimetric analyses were carried out on a NETZSCH STA 449C unit at a heating rate of  $15\text{ }^\circ\text{C}/\text{min}$  under a nitrogen atmosphere. X-ray powder diffraction (XRD) patterns ( $Cu\ K\alpha$ ) were collected on a Bruker Advance D8  $\theta\text{--}2\theta$  diffractometer.

#### 2.1.1. Synthesis of $[Zn_2(H_2L)_2] \cdot 2H_2O$ (**1**)

A mixture of  $ZnSO_4$  (0.35 mmol),  $H_4L$  (0.40 mmol) and ethanol (6 mL) as well as two drops of 10%  $N(CH_2CH_3)_3$  solution in 6 mL distilled water, was sealed into a Parr Teflon-lined autoclave (23 mL) and heated at  $120\text{ }^\circ\text{C}$  for 3 days. The final pH value was

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**Scheme 1.** The coordination modes of the diposponate ligand previously reported in references [7a–7c].

about 3.5 and the solid product, containing some unidentified white powder, was repeatedly rinsed with distilled water under ultrasonic treatment to obtain colorless plate-shaped crystals of **1**, in a ca. 78% yield based on Zn. Its purity has also been confirmed by powder XRD (see ESI, Fig. S1). *Anal. Calc.* for  $C_6H_{22}N_2O_{14}P_4Zn_2$  ( $M_r = 600.88$ ): C 11.99, H 3.69, N 4.66%. Found: C 11.93, H 3.77, N 4.60%. IR data (KBr,  $cm^{-1}$ ): 3397(s), 3103(m), 2917(m), 2712(m), 2282(m), 1647(m), 1475(m), 1412(m), 1306(m), 1217(m), 1192(s), 1167(vs), 1145(s), 1113(s), 1068(s), 1051(vs), 987(m), 972(m), 958(m), 903(m), 823(m), 735(m), 631(m) 580(m), 530(m), 504(m), 486(m), 467(m).

#### 2.1.2. Synthesis of $[Sr_3(H_2L)_2(H_3L)_2(H_2O)_2] \cdot 2H_2O$ (**2**)

A mixture of  $SrCl_2$  (0.40 mmol),  $H_4L$  (0.44 mmol) and ethanol (8 mL) as well as two drops of 10%  $N(CH_2CH_3)_3$  solution in 4 mL distilled water, was sealed into a Parr Teflon-lined autoclave (23 mL) and heated at 120 °C for 3 days. The final pH value was about 3.5 and colorless plate-shaped crystals of **2** were collected in a ca. 70% yield based on Sr. Its purity has also been confirmed by powder XRD (see ESI, Fig. S2). *Anal. Calc.* for  $C_{12}H_{46}N_4O_{28}P_8Sr_3$  ( $M_r = 1205.15$ ): C 11.96, H 3.85, N 4.65%. Found: C 11.89, H 3.95, N 4.58%. IR data (KBr,  $cm^{-1}$ ): 3386(s), 3122(m), 3072(m), 2971(m), 2734(m), 2551(m), 2345(m), 1645(m), 1476(m), 1406(m), 1317(m), 1273(s), 1205(vs), 1186(s), 1145(s), 1122(vs), 1087(s), 1012(s), 973(s), 920(s), 834(m), 712(m), 633(m), 606(m), 561(s), 524(m), 464(m), 446(m).

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

Compound	<b>1</b>	<b>2</b>
Empirical formula	$C_6H_{22}N_2O_{14}P_4Zn_2$	$C_{12}H_{46}N_4O_{28}P_8Sr_3$
Formula weight	600.88	1205.15
Space group	$P2_1/n$	$P-1$
$a$ (Å)	9.3581(3)	11.4592(5)
$b$ (Å)	8.9248(3)	12.5382(6)
$c$ (Å)	22.2825(6)	14.7512(7)
$\alpha$ (°)	90	104.981(1)
$\beta$ (°)	99.131(2)	108.132(1)
$\gamma$ (°)	90	91.356(1)
$V$ (Å <sup>3</sup> )	1837.43(10)	1933.16(16)
$Z$	4	2
$D_{calcd}$ ( $g\ cm^{-3}$ )	2.172	2.070
$\mu$ ( $mm^{-1}$ )	3.034	4.556
GOF on $F^2$	1.033	1.074
$R1, wR2$ [ $I > 2\sigma(I)$ ]	0.0257, 0.0629	0.0379, 0.0984
$R1, wR2$ (all data)	0.0330, 0.0660	0.0487, 0.1040

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR2 = \{ \sum w(F_o - F_c)^2 / \sum w(F_o)^2 \}^{1/2}.$$

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

<b>1</b>			
Zn(1)–O(12)	1.9994(15)	Zn(1)–O(3)#1	2.0192(16)
Zn(1)–O(4)	2.0271(15)	Zn(1)–O(1)	2.0929(16)
Zn(1)–O(7)#2	2.2262(16)	Zn(1)–O(9)	2.4019(16)
Zn(2)–O(2)	1.9388(16)	Zn(2)–O(9)	1.9449(15)
Zn(2)–O(8)#3	1.9527(16)	Zn(2)–O(11)#3	1.9635(16)
P(1)–O(3)	1.4947(16)	P(1)–O(2)	1.5214(17)
P(1)–O(1)	1.5304(15)	P(2)–O(6)	1.4831(16)
P(2)–O(4)	1.5153(17)	P(2)–O(5)	1.5800(17)
P(3)–O(7)	1.5025(17)	P(3)–O(8)	1.5172(16)
P(3)–O(9)	1.5392(16)	P(4)–O(12)	1.4930(17)
P(4)–O(11)	1.5068(17)	P(4)–O(10)	1.5503(16)
<b>Hydrogen bond</b>			
O(10)···O(2W)	2.498(3)	O(1W)···O(2W)#4	2.677(3)
O(2W)···O(5)#5	2.799(3)	O(6)···O(1W)	2.816(3)
N(2)···O(4)#3	2.723(3)	N(1)···O(3)	2.898(2)
<b>2</b>			
Sr(1)–O(3)#1	2.433(3)	Sr(1)–O(20)#2	2.434(3)
Sr(1)–O(11)	2.555(3)	Sr(1)–O(21)	2.566(3)
Sr(1)–O(15)	2.583(3)	Sr(1)–O(2)	2.603(3)
Sr(2)–O(9)	2.432(3)	Sr(2)–O(2W)	2.571(5)
Sr(2)–O(21)	2.594(3)	Sr(2)–O(17)#3	2.610(3)
Sr(2)–O(24)	2.627(3)	Sr(2)–O(15)	2.633(3)
Sr(2)–O(17)	2.646(3)	Sr(3)–O(18)	2.449(3)
Sr(3)–O(2)	2.533(3)	Sr(3)–O(11)	2.609(3)
Sr(3)–O(8)#4	2.620(3)	Sr(3)–O(8)	2.645(3)
Sr(3)–O(1W)	2.649(3)	Sr(3)–O(6)	2.675(3)
Sr(3)–O(15)	2.865(3)	P(1)–O(2)	1.485(3)
P(1)–O(3)	1.485(3)	P(1)–O(1)	1.569(4)
P(2)–O(5)	1.486(3)	P(2)–O(6)	1.509(3)
P(2)–O(4)	1.552(3)	P(3)–O(9)	1.480(3)
P(3)–O(8)	1.504(3)	P(3)–O(7)	1.575(3)
P(4)–O(10)	1.493(4)	P(4)–O(11)	1.503(3)
P(4)–O(12)	1.556(3)	P(5)–O(13)	1.504(3)
P(5)–O(14)	1.525(3)	P(5)–O(15)	1.525(3)
P(6)–O(18)	1.490(3)	P(6)–O(17)	1.506(3)
P(6)–O(16)	1.561(3)	P(7)–O(20)	1.490(3)
P(7)–O(21)	1.491(3)	P(7)–O(19)	1.555(4)
P(8)–O(22)	1.502(3)	P(8)–O(23)	1.509(3)
P(8)–O(24)	1.513(3)		
<b>Hydrogen bond</b>			
O(5)···O(4W)#4	2.732(5)	O(23)···O(4W)#5	2.734(5)
O(22)···O(3W)#3	2.760(5)	O(1W)···O(2W)#6	2.826(5)
N(2)···O(4W)	2.735(5)	N(4)···O(14)#2	2.760(6)
N(3)···O(3W)	2.792(5)	N(1)···O(12)#1	2.828(17)

#### Symmetry codes:

For **1**: #1  $-x+1/2, y-1/2, -z+1/2$ ; #2  $-x+3/2, y-1/2, -z+1/2$ ; #3  $-x+3/2, y+1/2, -z+1/2$ ; #4  $x+1/2, -y+1/2, z+1/2$ ; #5  $-x+1/2, y+1/2, -z+1/2$ .

For **2**: #1  $-x+1, -y, -z+1$ ; #2  $-x, -y, -z+1$ ; #3  $-x, -y+1, -z+1$ ; #4  $-x+1, -y+1, -z+1$ ; #5  $-x+1, -y+1, -z+2$ ;  $x+1, y, z$ .

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