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Metal diphosphonates with double-layer and pillared layered structures based on *N*-cyclohexylaminomethanediphosphonate

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ABSTRACT

Based on *N*-cyclohexylaminomethanediphosphonic acid (cmdpH$_4$), four new metal diphosphonate compounds with formula M_3(cmdpH)$_2$(H$_2$O)$_2$ [M=Zn(**1**), Co(**2**)] and M_2(cmdpH$_2$)$_2$(4,4′-bipy)$_{0.5}$(H$_2$O) [M=Co(**3**), Mn(**4**)] have been obtained and structurally determined. Compounds **1** and **2** are isostructural. Within the structure, the $M(2)O_6$ octahedra are each corner-shared with four PO$_3$C tetrahedra to form a single layer containing 3- and 7-member rings. Neighboring single layers are pillared by $M(1)O_4$ tetrahedra, resulting in a novel double-layer structure. The organic moieties of cmdpH^{3-} are grafted on the two sides of the double layer. Compounds **3** and **4** are also isostructural, displaying a pillared layered structure. Within the inorganic layer, the $M(1)O_5$ tetragonal pyramids and $M(2)NO_5$ octahedra are each linked by PO$_3$C tetrahedra through corner-sharing, forming a layer in the *ab* plane which contains 3- and 10-member rings. These layers are pillared by 4,4′-bipyridine via coordination with the $M(2)$ atoms from the adjacent layers, leading to a three-dimensional open framework structure with channels generated along the *a*-axis. The organic groups of cmdpH$_2^{2-}$ locate within the channels. Magnetic studies show that antiferromagnetic interactions are dominant in compounds **2–4**. Field dependent magnetization reveals a spin flop behavior for **2**.

1. Introduction

Metal phosphonate chemistry has attracted increasing research attention due to their potential applications in catalysts [1–7], optics [8,9], sorptions [10–15] and magnetic materials [16–21]. In the category of phosphonate, diphosphonates play important roles in bone disorder treatments for their strong affinity to metal ions [22–24]. It is found that diphosphonate drugs possessing a nitrogen atom in the organic backbone behave high inhibition activity. Moreover, the studies show that both the positively charged nitrogen atom and the nature and the size of the substitute groups on nitrogen atom are crucial for the compound activity. However, it is not well understood why small modifications in their structures lead to significant alterations in their biological characteristics [25]. Thus the structure–activity relationship study is desired to understand diphosphonate physiological activity. In the viewpoint of coordination chemistry, investigation of versatile coordination modes of the nitrogen-containing diphosphonates to different metal ions would be helpful in better understanding the above mentioned problems of mechanism.

Matczak-Jon reviewed the supramolecular chemistry and complexation abilities of diphosphonates in solution or solid state [26]. It is noticed that structural reports on metal diphosphonates involving (R_1)(R_2)NCH(PO$_3$H$_2$)$_2$ ligands (Scheme 1) are rather limited thus far. Compound Na$_4$[(O$_3$PCHN(CH$_3$)$_2$PO$_3$)W$_2$O$_6$]$\cdot$11H$_2$O contains negatively charged chains made up of corner-sharing WO$_6$ octahedra and (dimethy1amino)methylenediphosphonate (**L**^{1}) bridges. The Na$^+$ ions and water molecules locate in the space between the chains [27]. Based on aminomethylenediphosphonate (**L**^{2}), NaCo$_2${NH$_3$CH(PO$_3$)(PO$_3$H$_{0.5}$)}$_2$(H$_2$O)$_2\cdot x$H$_2$O was obtained showing an open framework structure in which the CoO$_6$ octahedra are bridged by PO$_3$C tetrahedra through vertex-sharing forming a layer containing 4- and 8-member rings. Neighboring layers are further connected by NaO$_6$ linkages [28]. While compound Na$_4$Zn{NH$_3$CH(PO$_3$)$_2$}$_2\cdot$4H$_2$O contains chains of [Zn{NH$_3$CH(PO$_3$)$_2$}$_2$]$_n^{4n-}$ made up of corner-sharing ZnO$_6$ octahedra and PO$_3$C tetrahedra, which are further connected by tetramers of edge-sharing NaO$_6$ octahedra. In the nickel compound Ni{NH$_3$CH(PO$_3$H)$_2$}$_2\cdot x$H$_2$O, a square-grid layer structure is found where the NiO$_6$ octahedra are corner-shared with PO$_3$C tetrahedra[29]. Apart from the transition metal compounds, lanthanide diphosphonates with 3D framework showing noninterpenetrated three-connected topology and 1D chain structure were also achieved through *N*-(2-pyridyl)-aminomethane-1,1-diphosphonic acid (**L**^{3}) [30]. Clearly a slight change of the organic tails (R_1 or R_2) leads to structural diverse

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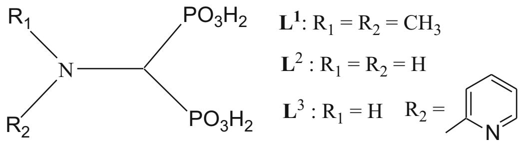
because the methyl and hydrogen as well as pyridyl groups hold different sizes and functions in the construction of metal diphosphonates. To better understand the influences of the substitute groups on the structures and properties of metal diphosphonates, we introduce a flexible cyclohexyl group into iminomethylenediphosphonate. *N*-cyclohexylaminomethanediphosphonic acid [$C_6H_{11}NHCH(PO_3H_2)_2$, *cmdp*H_4, Scheme 2a] is synthesized subsequently, based on which four new metal-cmdp compounds with formula $M_3(\text{cmdpH})_2(H_2O)_2$ [M=Zn(**1**), Co(**2**)] and $M_2(\text{cmdpH}_2)_2(\text{4,4-bpy})_{0.5}(H_2O)$ [M=Co(**3**), Mn(**4**)] are obtained. Compounds **1** and **2** show a novel double-layer structure, while compounds **3** and **4** exhibit a pillared layered structure. The magnetic properties of compounds **2–4** are also investigated.

2. Experimental section

2.1. Materials and methods

N-cyclohexylaminomethanediphosphonic acid [$C_6H_{11}NHCH(PO_3H_2)_2$, cmdpH_4] was prepared according to the literature method [31]. All the other starting materials were purchased commercially as reagent grade chemicals and used without further purification. The elemental analyses for C, H and N were performed in a PE240C elemental analyzer. The infrared spectra were recorded on a VECTOR 22 spectrometer with KBr pellets. Thermal analyses were performed in nitrogen with a heating rate of 10 °C/min on a TGA-DTA V1.1b Inst 2100 instrument. The powder XRD patterns were recorded on a Shimadzu XD-3A X-ray diffractometer. Magnetic susceptibility data of compounds **2–4** were obtained on microcrystalline samples (13.60 mg for **2**, 9.30 mg for **3** and 10.27 mg for **4**) using a Quantum Design MPMS-XL7 SQUID magnetometer. Diamagnetic corrections were made for both the sample holder and the compound estimated from Pascal's constants [32].



Scheme 1.

2.2. Syntheses

2.2.1. Synthesis of $Zn_3(\text{cmdpH})_2(H_2O)_2$ (**1**)

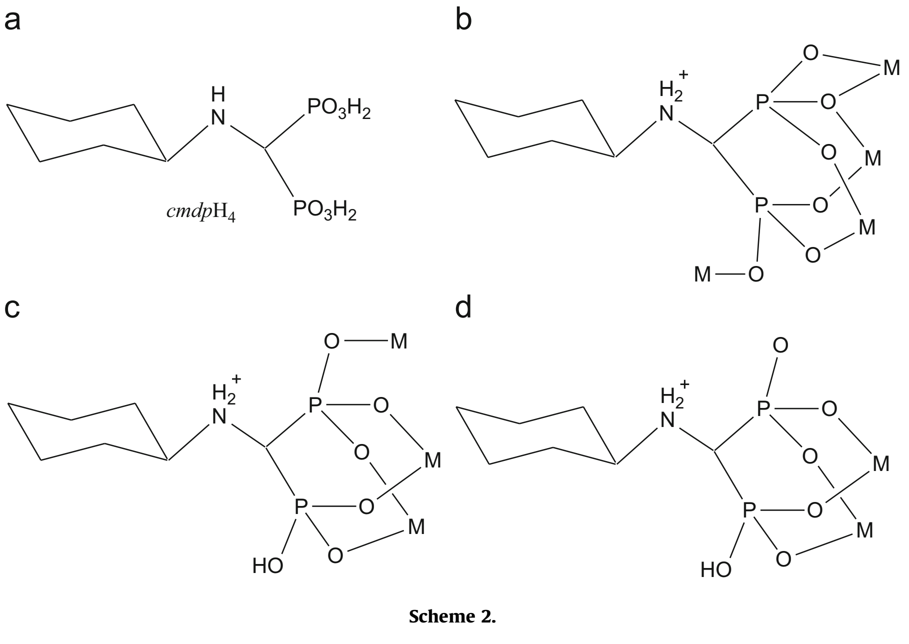
A mixture of $ZnSO_4\cdot 7H_2O$ (0.1 mmol, 0.0286 g), cmdpH_4 (0.1 mmol, 0.0310 g) and H_2O (8 cm^3), adjusted by 1 M NaOH to pH=2.5, was kept in a Teflon-lined autoclave at 140 °C for 72 h. After slow cooling to room temperature, the colorless lamellar crystals of compound **1** were collected as a monophasic material, judged by powder X-ray diffraction pattern. Yield: 60% based on Zn. Anal. Calcd. for $C_{14}H_{32}N_2O_{14}P_4Zn_3$: C, 21.75; H, 4.14; N, 3.62. Found: C, 20.74; H, 3.78; N, 3.46%. IR (KBr, cm^{-1}): 3439s, 3180m, 2935m, 2854m, 2554w, 1604m, 1458w, 1383m, 1114vs, 1066m, 968s, 775m, 556s. Thermal analysis reveals that the weight loss between 25 and 230 °C is 4.54%, in agreement with the removal of two coordinated water molecules (calcd. 4.66%).

2.2.2. Synthesis of $Co_3(\text{cmdpH})_2(H_2O)_2$ (**2**)

Compound **2** was prepared in a similar way to that of **1** except that $CoSO_4\cdot 7H_2O$ instead of $ZnSO_4\cdot 7H_2O$ was used as the starting material and the pH of the reaction mixture was adjusted to 3.5. Purple lamellar crystals were obtained as a monophasic material, judged by powder X-ray diffraction pattern. Yield: 65% based on Co. Anal. Calcd. for $C_{14}H_{32}N_2O_{14}P_4Co_3$: C, 22.32; H, 4.28; N, 3.72. Found: C, 22.45; H, 4.64; N, 4.10%. IR (KBr, cm^{-1}): 3386br, 3180m, 2933m, 2856m, 2557w, 1608s, 1458w, 1383m, 1128vs, 1031m, 954s, 782m, 561s. Thermal analysis reveals that the weight loss between 25 and 260 °C is 4.78%, in agreement with the removal of two coordinated water molecules (calcd. 4.78%).

2.2.3. Synthesis of $Co_2(\text{cmdpH}_2)_2(\text{4,4}'\text{-bipy})_{0.5}(H_2O)$ (**3**)

Hydrothermal treatment of a mixture of $CoSO_4\cdot 7H_2O$ (0.1 mmol, 0.0281 g), cmdpH_4 (0.1 mmol, 0.0310 g), 4,4′-bipyridine (0.1 mmol, 0.0156 g) and H_2O(8 cm^3), adjusted by 1 M NaOH to pH=3.2, at 180 °C for 48 h results in purple lamellar crystals of **3** as a monophasic material, judged by the powder X-ray diffraction pattern. Yield: 50% based on Co. Anal. Calcd. for $C_{19}H_{34}Co_2N_3O_{13}P_4$: C, 30.18; H, 4.79; N, 5.56. Found: C, 30.21; H, 4.67; N, 5.46%. IR (KBr, cm^{-1}): 3424br, 3024w, 2936m, 2855m,



Scheme 2.