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Sodium Cobalt Aminomethylidenediphosphonate with a Novel Open Framework Structure

Song-Song Bao,[†] Li-Min Zheng,[*,†] Yong-Jiang Liu,[†] Wei Xu,[‡] and Shouhua Feng[‡]

State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute,
Nanjing University, Nanjing 210093, P. R. China, and State Key Laboratory of Inorganic
Syntheses and Preparative Chemistry, Jilin University, Changchun 130023, P. R. China

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This paper reports the synthesis and crystal structure of a cobalt aminomethylenediphosphonate compound $NaCo_2\{NH_3CH(PO_3)(PO_3H_{0.5})\}_2(H_2O)_2\cdot xH_2O$ (**1**). It shows a novel open framework structure in which layers of $Co_2\{NH_3CH(PO_3)(PO_3H_{0.5})\}_2(H_2O)_2$ are connected by NaO_6 linkages. The magnetic studies show a dominant antiferromagnetic exchange between the Co(II) ions.

The exploration of porous materials based on metal phosphonates has been of great interest in recent years.[1] Among the various mono- or diphosphonate ligands studied so far, methylenediphosphonate (mdp, $O_3PCH_2PO_3$) and its derivatives [$O_3PC(R)(R')PO_3$] are unique due to their diversified coordination capabilities with metal ions. Such coordination capability arises from the single methyl group which separates the two phosphonate groups, and hence, the formation of stable six-member rings of M−O−P−C−P−O is favored. As a result, new structure types other than pillared layered are frequently observed for metal−mdp compounds including one-dimensional chains, two-dimensional layers, and three-dimensional framework structures.[2−7] In order to investigate the effect of the substituted groups on the structures of the corresponding metal methylenediphosphonate compounds, a systematic study has also been conducted in this lab on the basis of 1-hydroxyethylidenediphosphonate [hedp, $CH_3C(OH)(PO_3)_2$].[8,9] To explore new metal phosphonate materials with open-framework structures and functionalities, aminomethylenediphosphonate [amdp, $NH_2CH(PO_3)_2$] is employed because it contains a functional NH_2 group. In this paper, we report the synthesis and characterization of a Co−amdp compound, namely $NaCo_2\{NH_3CH(PO_3)(PO_3H_{0.5})\}_2(H_2O)_2\cdot xH_2O$ (**1**) which shows a novel open-framework structure. To the best of our knowledge, no example of metal−amdp compounds has been structurally determined, although the bonding properties of this ligand with metal ions such as UO_2^{2+}, In^{3+}, Ga^{3+}, Fe^{3+}, Gd^{3+}, and Nd^{3+} have been studied in solution.[10]

Compound **1** was synthesized by the hydrothermal treatment of a mixture of $Co(en)_3Cl_3\cdot 3H_2O$ (0.2 mmol, 0.079 g), $amdpH_4$ (0.6 mmol, 0.1142 g), 1 M NaOH (3 cm^3), and H_2O (5 cm^3), adjusted by 1 M HCl to pH ≈ 2.7, at 140 °C for 72 h. After slow cooling, needlelike purple-red crystals of **1** were obtained as a monophasic material.[11] The yield was 68% based on Co. Single crystal structural determination[12] revealed that compound **1** has a three-dimensional open-

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[*] To whom correspondence should be addressed. E-mail: lmzheng@netra.nju.edu.cn. Fax: +86-25-3314502.

[†] Nanjing University.

[‡] Jilin University.

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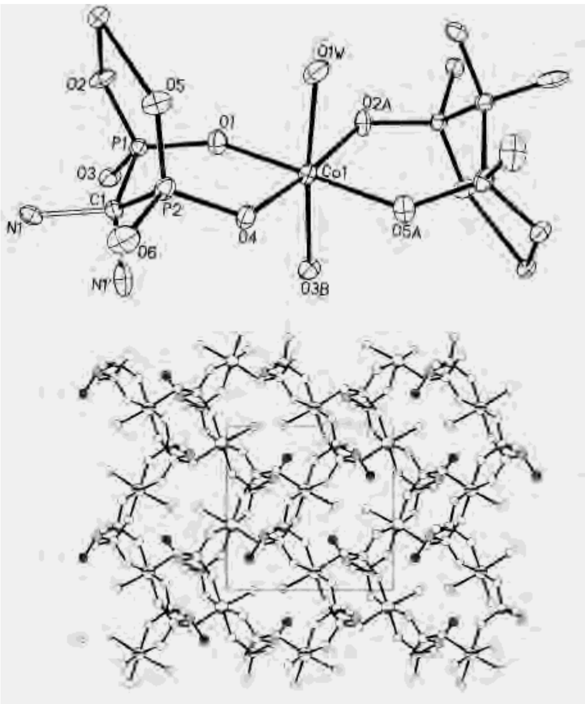

Figure 1. Top: Building unit of structure **1** (50% probability). Bottom: One layer of structure **1** viewed along the *a*-axis. All H and N1′ atoms are omitted for clarity.

framework structure composed of anionic layers with composition $Co^{II}\{NH_3CH(PO_3)(PO_3H_{0.5})\}(H_2O)$ and the $\{NaO_6\}$ linkages. As shown in Figure 1, each Co atom has a distorted octahedral environment with the four equatorial and one axial positions occupied by phosphonate oxygens [O(1), O(4), O(2A), O(5A), and O(3B)] from three equivalent amdp ligands. The sixth site is filled with a water molecule. The Co−O bond distances [2.055(4)−2.181(4) Å] and the O−Co−O bond angles [84.6(1)−177.8(1)°] are normal compared to those in the other cobalt phosphonates. The aminomethylenediphosphonate behaves as a zwitterionic bis(chelating) ligand and bridges the Co(II) ions into an infinite zigzag chain along the *c*-axis, using four of its six phosphonate oxygens [O(1), O(2), O(4), O(5)]. Neighboring chains are connected by vertex-sharing of the CoO_6 octahedra from one chain and the CPO_3 tetrahedra from the other via the phosphonate oxygen O(3), forming a two-dimensional undulating layer of $Co\{NH_3CH(PO_3)(PO_3H_{0.5})\}(H_2O)$ in the *bc*-plane which contains four- and eight-member rings (Figure 1). This layer may be compared with that in $[Fe_2(H_2O)_2(O_3PCH_2PO_3H)_2](H_2O)_2$.[7] The remaining phosphonate oxygen, O(6), is protonated [P(2)−O(6) 1.537(4) Å] and is involved in the interlayer hydrogen bonds [O(6)···O(6^i) (symmetry code: i, $-x$, y, $-z + {}^3/_2$): 2.522(8) Å]. The sodium atom, locating at a special site (0, 0.122545, 0.25), has a distorted octahedral environment. Four positions of each NaO_6 are occupied by phosphonate oxygens [O(4) or O(5)] from four equivalent amdp groups [average Na−O: 2.321(5) Å]. The remaining two positions are filled with lattice water [Na(1)−O(2w): 2.697(9) Å]. Consequently, the anionic layers of cobalt diphosphonate are connected through NaO_6 units, forming a three-dimensional open-framework with channels generated along the [001] direction (Figure 2). The lattice water resides in the channels. The protonated amino group and the coordinated water molecules point toward the channel.

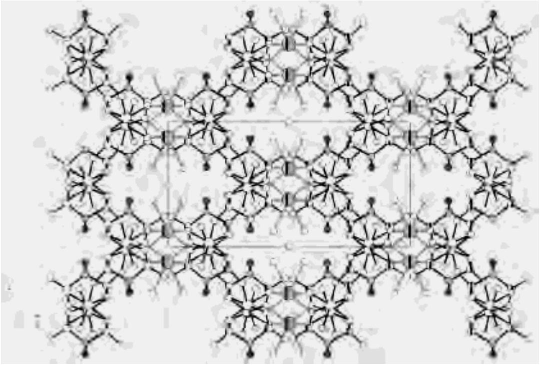

Figure 2. Structure **1** packed along the *c*-axis. All H and N1′ atoms are omitted for clarity.

The structure of compound **1** is clearly distinguished from those of $Na_3Co(O_3PCH_2PO_3)(\mu\text{-OH})$,[6] $Na_2Co(O_3PCH_2PO_3)\cdot H_2O$,[6] $Co_2(O_3PCH_2PO_3)(H_2O)$,[5] and $Na_6Co_7(hedp)_2(hedpH)_4(H_2O)_4\cdot 8H_2O$[9] where the $O_3PC(R)(R')PO_3$ ligand is employed. Compound $Na_3Co(O_3PCH_2PO_3)(\mu\text{-OH})$ has a chain structure in which the Co atoms are chelated and bridged by $O_3PCH_2PO_3$ ligands. In compound $Na_2Co(O_3PCH_2PO_3)\cdot H_2O$, a layer structure is found where equivalent chains of $\{Co(O_3PCH_2PO_3)\}_n$ are linked together by corner-sharing of CoO_5 square pyramids and CPO_3 tetrahedra. In compound $Co_2(O_3PCH_2PO_3)(H_2O)$, a purely inorganic framework is found with the organic moieties filling in the channel walls. In compound $Na_6Co_7(hedp)_2(hedpH)_4(H_2O)_4\cdot 8H_2O$, two types of chains with composition $\{Co_3(hedp)_2\}_n$ and $\{Co_2(hedpH)_2\}_n$ are cross-linked by corner-sharing of CoO_6 octahedra and CPO_3 tetrahedra, forming a layer between which the sodium ions reside.

Thermal analysis of **1** showed several steps of decomposition in the temperature range 50−600 °C. The weight loss below 210 °C is 6.8%, in agreement with the removal of two lattice water molecules (calcd 6.1%). The weight loss between 210 and 350 °C is 6.0%, corresponding to the release of two coordinated water molecules (calcd 6.1%). XRD patterns confirm that the framework structure is maintained after the removal of water molecules. The weight loss above 350 °C is due to the decomposition of the organophosphonate ligand and the collapse of the lattice structure. The final product was not characterized.

The temperature dependent molar magnetic susceptibilities of compound **1** were investigated in a magnetic field of 2

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(11) Anal. Found (Calcd) for $NaCo_2\{NH_3CH(PO_3)(PO_3H_{0.5})\}_2\ (H_2O)_2\cdot 2H_2O$: C, 3.48 (4.07); H, 3.19 (2.88); N, 4.05 (4.75)%. IR (KBr, cm^{-1}): 3448m, 3222br, 2949m, 2908m, 1637m, 1523m, 1333w, 1124s, 991m, 934m, 797m, 723w, 562m, 452w, 425w.

(12) Crystal data: $NaCo_2\{NH_3CH(PO_3)(PO_3H_{0.5})\}_2(H_2O)_2\cdot 1.4H_2O$, $M_r = 579.10$, monoclinic, space group $C2/c$, $a = 18.772(4)$ Å, $b = 9.417(2)$ Å, $c = 9.612(2)$ Å, $\beta = 102.593(4)°$, $V = 1658.4(6)$ Å^3, $Z = 4$, $D_c = 2.319$ g cm^{-3}, μ(Mo Kα) = 24.96 cm^{-1}, $\lambda = 0.71073$ Å. A crystal of dimensions 0.20 × 0.05 × 0.05 mm^3 was selected for indexing and intensity data collection at 298 K. Total number of measured and observed independent reflections ($I_0 > 2\sigma(I)$) are 5036, 1951 ($R_{int} = 0.0586$). Least-squares refinements were based on F^2 and converged at R1 = 0.0555, wR2 = 0.1241.

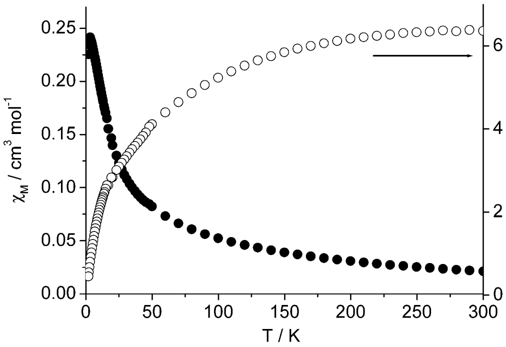

Figure 3. Temperature dependence of magnetic susceptibility of **1**.

kOe (Figure 3). The effective magnetic moment per Co at 300 K is 5.04 μ_B, much higher than the spin only value for spin $S = ^3/_2$ centers (3.87 μ_B) which is attributed to the significant orbital contribution of Co(II) ions. On cooling from room temperature, the χ_M value increases smoothly until reaching a maximum around 3.3 K, indicating a dominant antiferromagnetic interaction between the magnetic centers. This is confirmed by the continuous decreasing of $\chi_M T$ on cooling. The sharp drop of the $\chi_M T$ value below 25 K could be caused by the combined effect of both the antiferromagnetic exchange and the zero-field splitting of the single Co(II) ion. The magnetic susceptibility above 50.0 K obeys the Curie−Weiss law for **1** with a Weiss constant $\theta = -37$ K.

In summary, this paper reports the synthesis and structure of a new cobalt aminomethylenediphosphonate compound $NaCo_2\{NH_3CH(PO_3)(PO_3H_{0.5})\}_2(H_2O)_2 \cdot xH_2O$ (**1**). It shows a novel open-framework structure made up of $Co_2\{NH_3CH(PO_3)(PO_3H_{0.5})\}_2(H_2O)_2$ layers and NaO_6 linkages. The magnetic studies show a dominant antiferromagnetic exchange between the Co(II) ions.

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Supporting Information Available: Crystallographic file in CIF format. Additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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