

$\text{Co}_3\{\text{CH}_3\text{C}(\text{NH}_3)(\text{PO}_3\text{H})(\text{PO}_3)\}_2$ $\{\text{CH}_3\text{C}(\text{NH}_3)(\text{PO}_3\text{H})_2\}_2(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$: A cobalt 1-aminoethylidenediphosphonate with a layer structure

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Abstract

This paper describes the structure and magnetic properties of a novel cobalt 1-aminoethylidenediphosphonate compound, namely $\text{Co}_3\{\text{CH}_3\text{C}(\text{NH}_3)(\text{PO}_3\text{H})(\text{PO}_3)\}_2\{\text{CH}_3\text{C}(\text{NH}_3)(\text{PO}_3\text{H})_2\}_2(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$ (1). The structure contains a trimer unit of $\text{Co}_3\{\text{CH}_3\text{C}(\text{NH}_3)(\text{PO}_3\text{H})(\text{PO}_3)\}_2$ in which two equivalent phosphonate ligands chelate and bridge the three cobalt ions. Each trimer unit is further linked to its four equivalent neighbors through corner-sharing of CoO_6 octahedra and CPO_3 tetrahedra, forming a two-dimensional layer in the *bc*-plane which contains 12-membered rings. These layers are connected to each other by extensive hydrogen bonds. Magnetic studies show that weak antiferromagnetic interactions are mediated between the cobalt ions. Crystal data for 1: monoclinic, space group *C2/c*, $a = 27.727(4)$, $b = 7.1091(11)$, $c = 19.827(3)$ Å, $\beta = 118.488(3)$, $V = 3434.9(9)$ Å³, $Z = 2$.

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Keywords: Cobalt; Phosphonate; 1-aminoethylidenediphosphonate; Crystal structure; Magnetic

1. Introduction

In recent years, an increasing attention has been paid to the exploration of porous materials based on metal phosphonates [1]. The methylenediphosphonate (mdp, $\text{O}_3\text{PCH}_2\text{PO}_3$) and its derivatives [$\text{O}_3\text{PC}(\text{R})(\text{R}')\text{PO}_3$], among many other phosphonates, are powerful ligands in linking metal ions into a number of compounds with new structure types [2,3]. Previously, a systematic work about the template influences on the structures of transition metal-hedp compounds [hedp = 1-hydroxyethylidenediphosphonate, $\text{CH}_3\text{C}(\text{OH})(\text{PO}_3)_3$] has been conducted in this

lab, which resulted in a series of compounds with 1D, 2D and 3D structures [4]. A three-dimensional open framework structure was also achieved for $\text{NaCo}_2\{\text{NH}_3\text{CH}(\text{PO}_3)(\text{PO}_3\text{H}_{0.5})\}_2(\text{H}_2\text{O})_2 \cdot x\text{H}_2\text{O}$ where aminomethylenediphosphonate [amdp, $\text{NH}_2\text{CH}(\text{PO}_3)_2$] was employed [5]. In this paper, a related 1-aminoethylidenediphosphonate [aedp, $\text{CH}_3\text{C}(\text{NH}_2)(\text{PO}_3)_3$] ligand in which amino group replaces the hydroxy group in hedp was used to react with the cobalt salt under hydrothermal conditions. Compound $\text{Co}_3\{\text{CH}_3\text{C}(\text{NH}_3)(\text{PO}_3\text{H})(\text{PO}_3)\}_2\{\text{CH}_3\text{C}(\text{NH}_3)(\text{PO}_3\text{H})_2\}_2(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$ (1) with a novel layer structure has been prepared. Its magnetic behavior is investigated. As far as we are aware, no example of metal-aedp compounds has been structurally determined so far.

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2. Experimental

2.1. Materials and methods

The 1-aminoethylidenediphosphonic acid (aedpH₄) was prepared according to the literature [6]. All the other starting materials were of reagent grade quality and were obtained from commercial sources without further purification. The elemental analysis was performed in a PE240C elemental analyzer. The infrared spectrum was recorded on a VECTOR 22 spectrometer with pressed KBr pellets. Thermal analysis was performed in nitrogen in the temperature range 15–600 °C with a heating rate of 5 °C/min on a TGA-DTA V1.1b Inst 2100 instrument. The magnetic susceptibility data were obtained on polycrystalline sample (29.6 mg) using a MagLab System 2000 magnetometer.

2.2. Synthesis of $\text{Co}_3\{\text{CH}_3\text{C}(\text{NH}_3)(\text{PO}_3\text{H})(\text{PO}_3)\}_2\{\text{CH}_3\text{C}(\text{NH}_3)(\text{PO}_3\text{H})_2\}_2(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$ (**1**)

In a typical synthesis, a mixture of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.1175 g, 0.5 mmol), aedpH₄ (0.2057 g, 1.0 mmol) and 8 cm^3 H_2O (pH = 1.0) was kept in a Teflon-lined autoclave at 140 °C for 2 days. After slow cooling in air to room temperature, plate-like purple crystals of **1** were collected as a monophasic material, judged by the powder X-ray diffraction pattern. Yield: 82% based on Co. Found (calcd.) for $\text{C}_8\text{H}_{42}\text{N}_4\text{O}_{30}\text{P}_8\text{Co}_3$: C, 6.15 (8.74); H, 4.43 (3.82); N, 4.89 (5.10)%. IR (KBr, cm^{-1}): 3639sh, 3542sh, 2937b, 2530w, 2262w, 2086w, 1622m, 1546m, 1528m, 1453w, 1384w, 1260m, 1200–1052s, 995m, 948m, 925sh, 882w, 831w, 776sh, 654sh, 557sh. The same product can be obtained when the pH value of the reaction mixture was adjusted to 1.0–3.8 by 1 M NaOH. Thermal analysis revealed that compound **1** started to decompose at ca. 125 °C (Fig. 1).

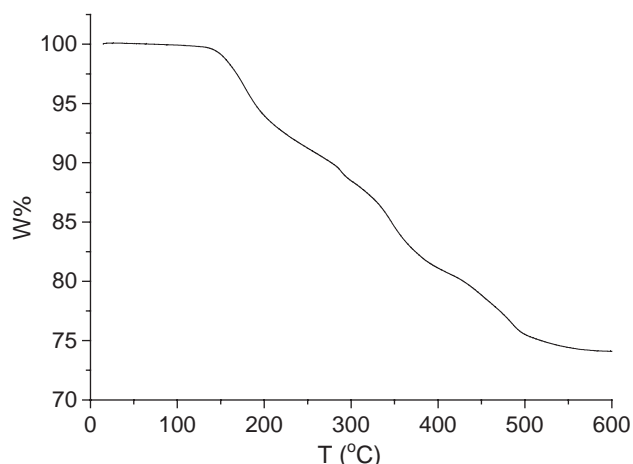


Fig. 1. TG curve of compound **1**.

The weigh loss below 260 °C is 9.3%, slightly lower than that calculated for the removal of six water molecules (9.8%). The residue at 600 °C is not characterized.

2.3. Crystallographic studies

A single crystal of dimensions $0.15 \times 0.10 \times 0.03$ mm for **1** was selected for indexing and intensity data collection at 298 K on a Bruker SMART APEX CCD diffractometer equipped with graphite-monochromatized $\text{MoK}\alpha$ ($\lambda = 0.71073$ Å) radiation. A hemisphere of data was collected in the θ range 1.67 – 25.0° using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 10 s/frame. Numbers of measured and observed reflections [$I > 2\sigma(I)$] are 10427 and 3014 ($R_{\text{int}} = 0.1021$), respectively. The data were integrated using the Siemens SAINT program [7], with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. Empirical absorption and extinction corrections were applied.

The structure was solved by direct method and refined on F^2 by full-matrix least squares using SHELXTL [8]. All the non-hydrogen atoms in compound **1** were refined anisotropically. All the hydrogen atoms were put on calculated positions or located from the Fourier maps and refined isotropically with the isotropic vibration parameters related to the non-H atom to which they are bonded. In the final Fourier-difference map the deepest hole and the highest peak were -0.688 and $0.796 \text{ e}\text{\AA}^{-3}$, respectively. The CCDC reference number for compound **1** is 257341. Crystallographic and refinement details are listed in Table 1. The atomic coordinates and selected bond lengths and angles are given in Tables 2 and 3, respectively.

Table 1
Crystallographic data for **1**

Formula	$\text{C}_8\text{H}_{42}\text{Co}_3\text{N}_4\text{O}_{30}\text{P}_8$
M	1099.01
Crystal system	Monoclinic
Space group	$C2/c$
$a/\text{\AA}$	27.727(4)
$b/\text{\AA}$	7.1091(11)
$c/\text{\AA}$	19.827(3)
$\beta/^\circ$	118.488(3)
$V/\text{\AA}^3$	3434.9(9)
Z	2
$D_c/\text{g/cm}^3$	2.125
$F(000)$	2236
Goodness-of-fit on F^2	1.040
$R1, wR2^a$ [$I > 2\sigma(I)$]	0.0654, 0.1238
(All data)	0.1120, 0.1367
Extinction coefficient/ mm^{-1}	0.00095(15)
$(\Delta\rho)_{\text{max}}, (\Delta\rho)_{\text{min}}/\text{e}\text{\AA}^{-3}$	0.796, -0.688

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

Table 2
Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for **1**

Atom	x	y	z	U(eq) ^a
Co(1)	0.1664(1)	0.4622(2)	0.1419(1)	0.013(1)
Co(2)	0.2500	0.2500	0.5000	0.013(1)
P(1)	0.0757(1)	0.4592(3)	-0.0483(1)	0.017(1)
P(2)	0.0738(1)	0.1433(3)	0.0480(1)	0.015(1)
P(3)	0.2311(1)	0.2644(3)	0.3285(1)	0.012(1)
P(4)	0.2290(1)	-0.1199(3)	0.3882(1)	0.012(1)
O(1)	0.1046(2)	0.5438(7)	0.0307(3)	0.017(1)
O(2)	0.0980(2)	0.5119(7)	-0.1009(3)	0.026(2)
O(3)	0.0126(2)	0.4972(8)	-0.0876(3)	0.026(2)
O(4)	0.1237(2)	0.2094(7)	0.1180(3)	0.014(1)
O(5)	0.0198(2)	0.2245(7)	0.0340(3)	0.017(1)
O(6)	0.0736(2)	-0.0759(7)	0.0516(3)	0.019(1)
O(7)	0.2223(2)	0.3664(7)	0.3889(3)	0.014(1)
O(8)	0.2103(2)	0.3752(7)	0.2549(3)	0.015(1)
O(9)	0.2903(2)	0.2016(7)	0.3574(3)	0.017(1)
O(10)	0.2384(2)	-0.0203(7)	0.4599(3)	0.018(1)
O(11)	0.2795(2)	-0.1889(7)	0.3852(3)	0.015(1)
O(12)	0.1877(2)	-0.2858(7)	0.3707(3)	0.018(1)
N(1)	0.1392(3)	0.1577(10)	-0.0213(4)	0.015(2)
N(2)	0.1881(3)	-0.0391(10)	0.2369(4)	0.014(2)
C(1)	0.0814(3)	0.2030(10)	-0.0364(4)	0.012(2)
C(2)	0.0414(3)	0.0978(12)	-0.1091(4)	0.025(2)
C(3)	0.1914(3)	0.0433(11)	0.3077(4)	0.012(2)
C(4)	0.1331(3)	0.0786(11)	0.2942(4)	0.020(2)
O(1W)	0.1185(2)	0.6356(8)	0.1735(3)	0.019(1)
O(2W)	0.1699(2)	0.2267(7)	0.4864(3)	0.018(1)
O(3W)	0.0644(3)	0.5638(14)	0.2493(4)	0.070(3)

^aU(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

3. Results and discussion

3.1. Structural description

Compound **1** crystallizes in monoclinic space group $C2/c$. Fig. 2 shows the building unit of the structure with atomic labeling scheme. Clearly, there are two crystallographically distinguished cobalt atoms, each has a distorted octahedral coordination geometry. The Co(1) atom locates at a general position. Five of its binding sites are provided by phosphonate oxygens [O(1), O(4), O(8), O(9A), O(11A)] from three aedp groups. The sixth site is filled with a water molecule [O(1W)]. The Co(2) atom sits at a special position (0.25, 0.25, 0.5). The basal plane of each Co(2)O_6 octahedron is occupied by four phosphonate oxygens [O(7), O(7B), O(10), O(10B)] from two equivalent aedp groups. The two axial positions are occupied by oxygen atoms from two water molecules. The Co–O bond lengths fall in the range of 2.046(5)–2.127(5) Å, in agreement with those in the other cobalt phosphonate compounds [2c,3,5,9–11]. The O–Co–O angles [80.8(2)–174.0(2)°] are normal.

Two types of 1-aminoethylidenediphosphonate ligand are found in the structure. One serves as a zwitterion

Table 3
Selected bond lengths (\AA) and angles (deg) for **1**

Co(1)–O(8)	2.070(5)	Co(1)–O(4)	2.078(5)
Co(1)–O(9A)	2.080(5)	Co(1)–O(11A)	2.114(5)
Co(1)–O(1W)	2.114(5)	Co(1)–O(1)	2.127(5)
Co(2)–O(10)	2.046(5)	Co(2)–O(2W)	2.112(5)
Co(2)–O(7)	2.125(5)	P(1)–O(2)	1.491(6)
P(1)–O(1)	1.505(5)	P(1)–O(3)	1.564(6)
P(2)–O(4)	1.493(5)	P(2)–O(5)	1.502(5)
P(2)–O(6)	1.560(5)	P(3)–O(8)	1.510(5)
P(3)–O(7)	1.515(5)	P(3)–O(9)	1.525(5)
P(4)–O(10)	1.495(5)	P(4)–O(11)	1.510(5)
P(4)–O(12)	1.564(5)		
O(8)–Co(1)–O(4)	88.01(19)	O(8)–Co(1)–O(9A)	101.4(2)
O(4)–Co(1)–O(9A)	166.8(2)	O(8)–Co(1)–O(11A)	90.04(19)
O(4)–Co(1)–O(11A)	84.2(2)	O(9A)–Co(1)–O(11A)	86.5(2)
O(8)–Co(1)–O(1W)	88.9(2)	O(4)–Co(1)–O(1W)	101.7(2)
O(9A)–Co(1)–O(1W)	87.9(2)	O(11A)–Co(1)–O(1W)	174.0(2)
O(8)–Co(1)–O(1)	166.0(2)	O(4)–Co(1)–O(1)	84.89(19)
O(9A)–Co(1)–O(1)	87.8(2)	O(11A)–Co(1)–O(1)	101.17(19)
O(1W)–Co(1)–O(1)	80.8(2)	O(2WB)–Co(2)–O(7)	86.59(19)
O(10)–Co(2)–O(2WB)	94.8(2)	O(2W)–Co(2)–O(7)	93.41(19)
O(10)–Co(2)–O(2W)	85.2(2)	O(10)–Co(2)–O(7)	92.88(19)
O(10)–Co(2)–O(7B)	87.12(19)	P(1)–O(1)–Co(1)	137.4(3)
P(2)–O(4)–Co(1)	131.1(3)	P(3)–O(7)–Co(2)	121.2(3)
P(3)–O(8)–Co(1)	163.5(3)	P(3)–O(9)–Co(1C)	139.2(3)
P(4)–O(11)–Co(1C)	129.0(3)	P(4)–O(10)–Co(2)	137.6(3)

Symmetry transformations used to generate equivalent atoms: A: $-x+1/2, y+1/2, -z+1/2$; B: $-x+1/2, -y+1/2, -z+1$; C: $-x+1/2, y-1/2, -z+1/2$.

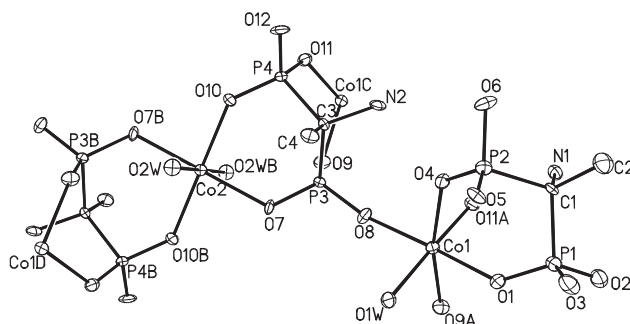


Fig. 2. Building unit of structure **1** with the atomic labeling scheme (thermal ellipsoids shown at 50% probability). Symmetry codes: A: $-x+1/2, y+1/2, -z+1/2$; B: $-x+1/2, -y+1/2, -z+1$; C: $-x+1/2, y-1/2, -z+1/2$; D: $x, -y+1, z+1/2$.

terminal ligand and chelates Co(1) atom using phosphonate oxygens O(1) and O(4). The remaining four phosphonate oxygens are either protonated [P(1)–O(3): 1.564(6), P(2)–O(6): 1.560(5) Å] or pendant [P(1)–O(2): 1.491(6), P(2)–O(5): 1.502(5) Å]. The other type of 1-aminoethylidenediphosphonate behaves as a zwitterion bis(chelating) bridging ligand, and bridges the Co(1) and Co(2) atoms via four of its six phosphonate oxygens [O(7), O(9), O(10), O(11)], forming a trimer of $\text{Co}_3\{\text{CH}_3\text{C}(\text{NH}_3)(\text{PO}_3\text{H})(\text{PO}_3)\}_2$ (Fig. 2). One of the remaining phosphonate oxygens [O(8)] is coordinated to the Co(1) atom of the neighboring trimer. The O(12)

atom is protonated [P(4)–O(12): 1.564(5) Å]. As a consequence, each $\text{Co}_3\{\text{CH}_3\text{C}(\text{NH}_3)(\text{PO}_3\text{H})(\text{PO}_3)\}_2$ trimer is connected to four other equivalent trimers through vertex-sharing of $\{\text{Co}(1)\text{O}_6\}$ octahedra from one trimer and $\{\text{CPO}_3\}$ tetrahedra from the other through O(8) atom, leading to a layer of $[\text{Co}_3\{\text{CH}_3\text{C}(\text{NH}_3)(\text{PO}_3\text{H})(\text{PO}_3)\}_2\{\text{CH}_3\text{C}(\text{NH}_3)(\text{PO}_3\text{H})_2\}_2(\text{H}_2\text{O})_4]_n$ in approximately the bc -plane which contains 12-membered rings (Fig. 3). The adjacent layers are connected by strong inter-layer hydrogen bonds, resulting in a three-dimensional supramolecular network structure with channels (Fig. 4). The shortest contacts between the layers are 2.551(7), 2.600(7) and 2.614(7) Å for O(3)...O(5ⁱ), O(6)...O(5ⁱⁱ) and O(12)...O(7ⁱⁱⁱ) (symmetry code: i, $-x, -y+1, -z$; ii, $-x, -y, -z$; iii, $x, y-1, z$), respectively. The lattice water molecules reside in the channels.

It is worth noting that the structure of compound **1** is unique comparing with the other cobalt compounds containing related phosphonate ligands. For those containing methylenediphosphonate, $\text{Na}_3\text{Co}(\text{O}_3\text{PCH}_2\text{PO}_3)(\mu\text{-OH})$ has a chain structure in which the Co atoms are chelated and bridged by $\text{O}_3\text{PCH}_2\text{PO}_3$ ligands

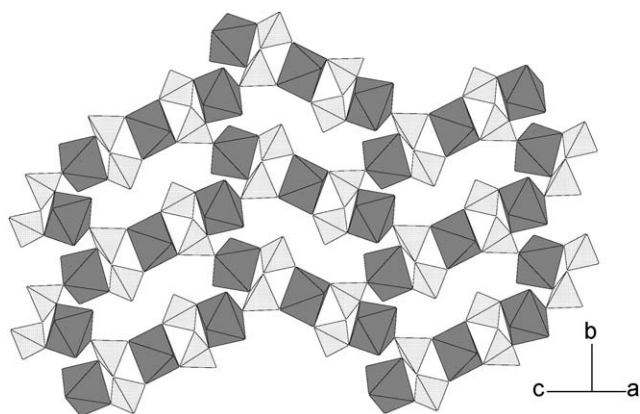


Fig. 3. Polyhedral representation of one layer of structure **1**. Codes: $\{\text{CoO}_6\}$, grey octahedron; $\{\text{CPO}_3\}$, dotted tetrahedron.

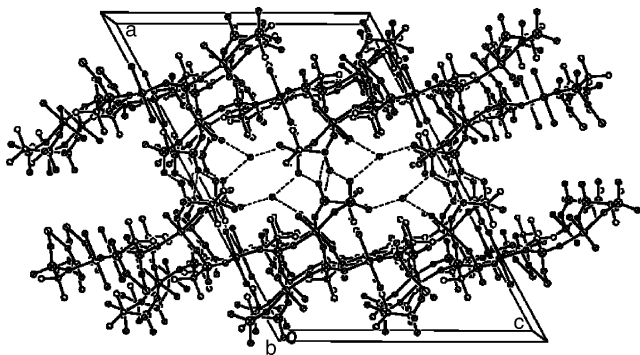


Fig. 4. Crystal packing of compound **1** viewed along b -axis. The hydrogen atoms are omitted for clarity.

[3]. Compound $\text{Na}_2\text{Co}(\text{O}_3\text{PCH}_2\text{PO}_3) \cdot \text{H}_2\text{O}$ has a layer structure where equivalent chains of $\{\text{Co}(\text{O}_3\text{PCH}_2\text{PO}_3)\}_n$ are linked by corner-sharing of CoO_5 square pyramids and CPO_3 tetrahedra [3]. Compound $\text{Co}_2(\text{O}_3\text{PCH}_2\text{PO}_3)(\text{H}_2\text{O})$ has a purely inorganic framework structure with the organic moieties filling in the channel walls [2c]. For those containing 1-hydroxyethylidenediphosphonate such as $\text{Na}_6\text{Co}_7(\text{hedp})_2(\text{hedpH})_4(\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}$ [9], $(\text{NH}_4)_2\text{Co}_2(\text{hedpH})_2$ [10] and $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{Co}_2(\text{hedpH})_2 \cdot 2\text{H}_2\text{O}$ ($n = 4, 5$) [11] with layer or chain structures, the hydroxy groups are all involved in the coordinations to the Co(II) ions. In compound $\text{NaCo}_2\{\text{NH}_3\text{CH}(\text{PO}_3)(\text{PO}_3\text{H}_{0.5})\}_2(\text{H}_2\text{O})_2 \cdot x\text{H}_2\text{O}$ [5], the aminomethylenediphosphonate behaves as a zwitterion bis(chelating) ligand and bridges the Co(II) ions into a two-dimensional undulating layer which contains four- and eight-member rings.

3.2. Magnetic properties

The temperature-dependent molar magnetic susceptibilities of compound **1** were investigated in a magnetic field of 20 kOe (Fig. 5). The effective magnetic moment per Co at 300 K is $5.07\mu_{\text{B}}$, higher than the spin only value for spin $S = 3/2$ centers ($3.87\mu_{\text{B}}$). This can be attributed to the significant orbital contribution of Co(II) ions. On cooling down from room temperature, the $\chi_{\text{M}}T$ value decreases continuously indicating weak antiferromagnetic interactions between the Co(II) centers. This is confirmed by the negative Weiss constant ($\theta = -13\text{ K}$), determined by the magnetic susceptibility data above 100 K (Fig. 5). According to the structure described above, the Co(II) ions are connected to each other purely through the O–P–O bridges within the layer. The weak antiferromagnetic interaction should be propagated through the O–P–O linkages. Similar phenomenon has been observed in $\text{NaCo}_2\{\text{NH}_3\text{CH}(\text{PO}_3)(\text{PO}_3\text{H}_{0.5})\}_2(\text{H}_2\text{O})_2 \cdot x\text{H}_2\text{O}$ [5].

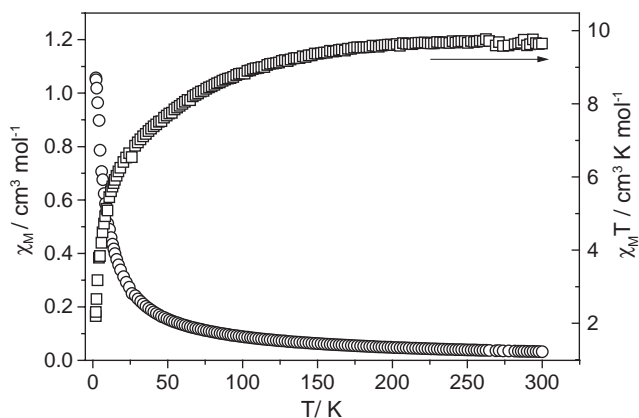


Fig. 5. χ_{M} and $\chi_{\text{M}}T$ versus T plots for compound **1**.

4. Conclusions

This paper reports the hydrothermal synthesis and characterization of a new cobalt diphosphonate compound $\text{Co}_3\{\text{CH}_3\text{C}(\text{NH}_3)(\text{PO}_3\text{H})(\text{PO}_3)\}_2\{\text{CH}_3\text{C}(\text{NH}_3)(\text{PO}_3\text{H})_2\}_2(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$. It displays a unique layer structure containing 12-membered rings, which are built up from the distorted $\{\text{CoO}_6\}$ octahedra and $\{\text{CPO}_3\}$ tetrahedra through vertex-sharing. Weak antiferromagnetic interactions are propagated between the Co(II) centers.

Acknowledgments

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