

Syntheses, structure and magnetic properties of pillared layered diphosphonates: $M_2(O_3PC_6H_4PO_3)(H_2O)_2$ ($M = Co^{II}$, Ni^{II})[☆]

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Abstract

This paper describes the hydrothermal syntheses of two isostructural metal bisphosphonates: $M_2(O_3PC_6H_4PO_3)(H_2O)_2$ [$M = Co^{II}$ (**1**), Ni^{II} (**2**)]. Single-crystal structure determination of compound **1** revealed a pillared layered structure in which the phenyl groups connect the inorganic layers of cobalt phosphonate. Crystal data for **1**: orthorhombic, space group $Pnmm$, $a = 19.306(5)$, $b = 4.8293(12)$, $c = 5.6390(14)$ Å, $V = 525.7(2)$ Å³, $Z = 2$. Magnetic susceptibility data indicate that antiferromagnetic interactions are mediated in both cases.

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Keywords: Cobalt; Nickel; Phosphonate; 1,4-phenylenebisphosphonic acid; Crystal structure; Magnetic property

1. Introduction

Metal phosphonate compounds have attracted substantial research interest primarily because of their potential applications in sorption and ion exchange, catalysis, sensors and nonlinear optics [1–6]. A number of compounds with layered or pillared layered structures have been prepared and crystallographically characterized since the first structure was solved by Mallouk et al. [7,8]. However, by using phenylbisphosphonic acid, only two compounds $Zn_2(O_3PC_6H_4PO_3)(H_2O)_2$ [9] and $Cu_2(O_3PC_6H_4PO_3)(H_2O)_2$ [10] have been synthesized. Their structures were determined through powder X-ray diffraction method.

In this paper, we report two new isostructural compounds based on phenylbisphosphonate, namely $Co_2(O_3PC_6H_4PO_3)(H_2O)_2$ (**1**) and $Ni_2(O_3PC_6H_4PO_3)(H_2O)_2$ (**2**). Single crystal structure determination reveals that structure **1** is analogous to that of $Zn_2(O_3PC_6H_4PO_3)(H_2O)_2$ [9]. The magnetic properties of both compounds have been investigated.

2. Experimental

2.1. Materials and methods

The 1,4-phenylenebisphosphonic acid was prepared according to the literature [11]. All the other starting materials were of reagent quality and were obtained from commercial sources without further purification. Elemental analyses were performed on a Perkin Elmer 240C elemental analyzer. IR spectra were obtained as KBr disks on a VECTOR 22 spectrometer. Variable-temperature magnetic susceptibility data for **1** and **2** were obtained on polycrystalline samples from 2 to 300 K in a magnetic field of 10 kG using a MagLab System 2000 magnetometer. Diamagnetic corrections were estimated from Pascal's constants [12].

2.2. Synthesis of $Co_2(O_3PC_6H_4PO_3)(H_2O)_2$ (**1**)

A mixture of $Co(en)_3Cl_3$ (0.3 mmol, 0.1200 g), 1,4-phenylenebisphosphonic acid (0.3 mmol, 0.0714 g) in 8 mL H_2O , adjusted to pH = 3–4 with 1 M NaOH, was kept in a Teflon-lined autoclave at 140°C for 54 h. After slow cooling to room temperature, purple-red lamellar crystals were collected as a monophasic material, based on the powder X-ray diffraction pattern. Yield: 0.036 g

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(62% based on Co). Anal. found (calcd) for $C_6H_8Co_2O_8P_2$: C, 19.05 (18.55); H, 2.48 (2.08)%. IR (KBr, cm^{-1}): 3425 s, 1613 s, 1385 w, 1156 s, 1110 s, 967 s, 828 w, 686 w, 625 m, 594 m.

2.3. Synthesis of $Ni_2(O_3PC_6H_4PO_3)(H_2O)_2$ (**2**)

A mixture of $NiSO_4 \cdot 6H_2O$ (0.2 mmol, 0.0525 g), 1,4-phenylenebisphosphonic acid (0.2 mmol, 0.0476 g) in 8 mL H_2O , adjusted to pH = 3–4 with 1 M NaOH, was kept in a Teflon-lined autoclave at 140°C for 54 h. After slow cooling to room temperature, light green crystals were obtained as a monophasic material, based on the powder X-ray diffraction pattern. Yield: 0.025 g (65% based on Ni). Anal. found (calcd) for $C_6H_8Ni_2O_8P_2$: C, 17.82 (18.59); H, 2.31 (2.08)%. IR (KBr, cm^{-1}): 3448 s, 1630 s, 1385 w, 1159 s, 1102 s, 978 s, 828 w, 743 w, 633 m, 597 m.

2.4. Crystallographic studies

A single crystal of dimensions $0.20 \times 0.08 \times 0.05$ 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 $MoK\alpha$ ($\lambda = 0.71073$ Å) radiation. A hemisphere of data was collected in the θ range 2.11–26.79° using a narrow-frame method with scan widths of 0.30° in ω and exposure time of 10 s/frame. Number of measured and observed reflections [$I > 2\sigma(I)$] are 3064 and 636 ($R_{int} = 0.0625$), respectively. The data were integrated using the Siemens SAINT program [13], 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 [14].

Table 1
Crystallographic data for **1**

Formula	$C_6H_8Co_2O_8P_2$
M	387.92
Crystal system	Orthorhombic
Space group	$Pnmm$
a (Å)	19.306(5)
b (Å)	4.8293(12)
c (Å)	5.6390(14)
V (Å ³)	525.7(2)
Z	2
D_c (g cm ⁻³)	2.450
$F(000)$	384
Goodness-of-fit on F^2	1.101
$R_1, wR_2 [I > 2\sigma(I)]$	0.0479, 0.1268
(All data)	0.0547, 0.1304
Extinction coefficient (mm ⁻¹)	0.016(4)
$(\Delta\rho)_{max}, (\Delta\rho)_{min}$ (e Å ⁻³)	2.096, -0.691

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

Table 2

Atomic coordinates and equivalent isotropic displacement parameters for **1**

	x/a	y/b	z/c	U_{eq}
Co(1)	0.2391(1)	0.3448(2)	0	0.014(1)
P(1)	0.3358(1)	0.9105(3)	0	0.011(1)
O(1)	0.3233(2)	0.6030(9)	0	0.017(1)
O(2)	0.3041(1)	1.0579(6)	0.2170(5)	0.014(1)
O(1W)	0.1581(3)	0.0506(11)	0	0.020(1)
C(1)	0.4278(3)	0.9659(13)	0	0.015(1)
C(21)	0.4637(5)	0.9830(20)	0.2125(17)	0.021(2)
C(22)	0.4556(12)	1.2210(50)	0	0.069(7)
C(23)	0.4706(13)	0.7460(50)	0	0.066(6)

U_{eq} is defined as one-third of the trace of the orthogonalized, U_{ij} tensor.

Table 3

Selected bond lengths (Å) and angles (deg) for **1**

Co(1)–O(1)	2.049(4)	P(1)–O(1)	1.504(5)
Co(1)–O(2A)	2.074(3)	P(1)–O(2)	1.543(3)
Co(1)–O(1W)	2.114(5)	P(1)–C(1)	1.796(6)
Co(1)–O(2C)	2.234(3)		
O(1)–Co(1)–O(2A)	90.99(12)	O(2A)–Co(1)–O(2D)	96.44(7)
O(2A)–Co(1)–O(2B)	100.59(17)	O(2C)–Co(1)–O(2D)	66.44(15)
O(1)–Co(1)–O(1W)	175.25(19)	O(1)–Co(1)–O(2D)	86.09(13)
O(2A)–Co(1)–O(1W)	92.04(12)	Co(1G)–O(2)–Co(1F)	120.22(13)
O(1)–Co(1)–O(2C)	86.09(13)	P(1)–O(2)–Co(1F)	94.28(14)
O(2A)–Co(1)–O(2C)	162.77(14)	P(1)–O(1)–Co(1)	136.7(3)
O(2B)–Co(1)–O(2C)	96.44(7)	P(1)–O(2)–Co(1G)	122.75(18)
O(1W)–Co(1)–O(2C)	89.93(14)		

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

The non-hydrogen atoms were refined anisotropically except the C(21), C(22) and C(23) atoms of the disordered phenyl group. The latter atoms as well as the H atoms attached to O(1W) were refined isotropically. The H atoms related to the disordered carbon atoms of the phenyl group are not located. In the final Fourier difference map, the deepest hole was $-0.691 e \text{ \AA}^{-3}$, and the highest peak was $2.096 e \text{ \AA}^{-3}$ [1.52 \AA from Co(1)]. 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.

3. Results and discussion

3.1. Structural description

Compound **1** has a pillared layered structure. Fig. 1 shows the building unit of the structure. The Co atom has a distorted octahedral environment. Five of the six coordination sites are occupied by the phosphonate oxygens from four equivalent $\{CPO_3\}$ groups. The sixth

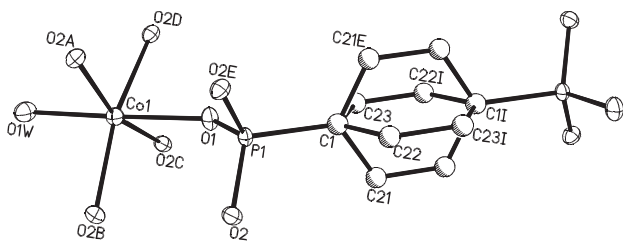


Fig. 1. Building unit of structure **1** with the atomic labeling scheme (thermal ellipsoids shown at 50% probability except for the C atoms).

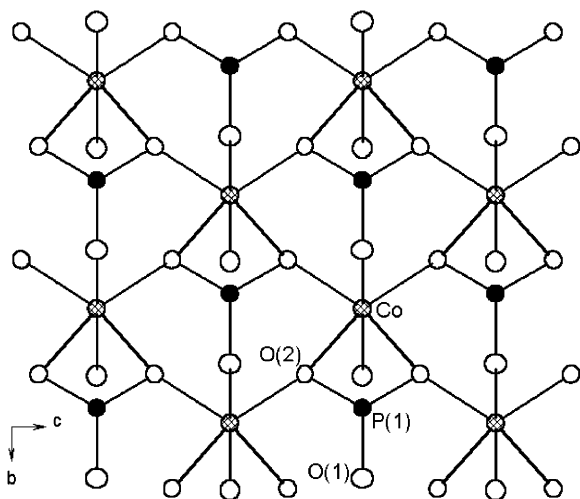


Fig. 2. One inorganic layer of structure **1**.

site is filled with a water molecule. The Co–O bond lengths are in the range 2.049(4)–2.234(3) Å, comparable to those in the other cobalt phosphonates [15]. Each {CPO₃} tetrahedron is connected to four {CoO₆} octahedral through corner- or edge-sharing, forming an inorganic layer (Fig. 2). One of the three phosphonate oxygens [O(1)] coordinates to a single cobalt atom, trans to the water molecule [O(1W)]. The O(1)–Co(1)–O(1W) angle is 175.25(19)°. The other two phosphonate oxygens [O(2), O(2E)] are related by a mirror plane. Each serves as a μ_3 -O bridge linking two equivalent Co atoms. Consequently, the O(2C)–Co(1)–O(2D) angle is small [66.44(15)°] compared with the other O–Co–O angles [86.09(13)–175.25(19)°] due to the formation of a four member ring of {P–O–Co–O}. The P(1)–O(2) bond length [1.543(3) Å] is longer than that of P(1)–O(1) [1.504(5) Å].

The inorganic layers are linked by the phenyl groups of the diphosphonate ligand, resulting in a pillared layered structure (Fig. 3). The phenyl group is disordered over two orientations, similar to those observed in compounds $M(\text{C}_6\text{H}_5\text{PO}_3)(\text{H}_2\text{O})$ ($M = \text{Mn}, \text{Zn}$) [7,16] and $\text{Zn}_2(\text{O}_3\text{PC}_6\text{H}_4\text{PO}_3)(\text{H}_2\text{O})_2$ [9]. The interlayer distance is about 6.3 Å. The distances between adjacent phenyl rings along *b*- and *c*-axis are ca. 4.8 and 5.6 Å, respectively, by calculating the distances between

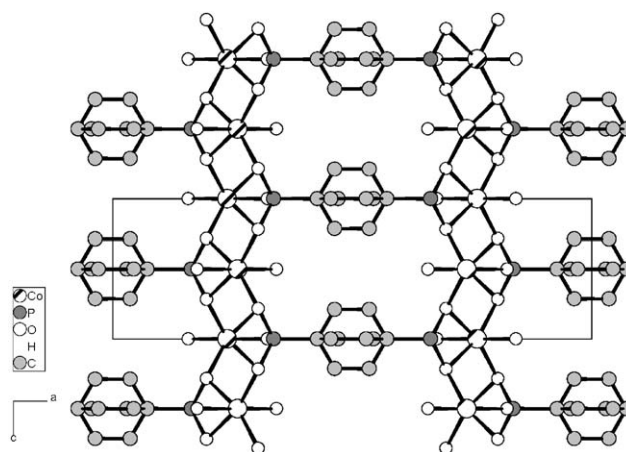


Fig. 3. Crystal packing of structure **1** viewed along *a*-axis.

adjacent P atoms. No π – π interactions should exist between the phenyl rings.

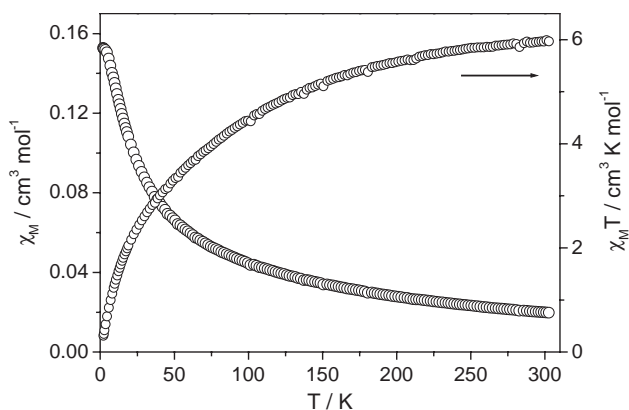
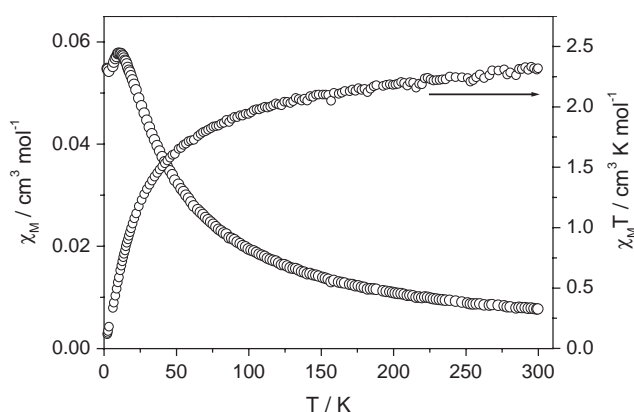
Compound **2** is isostructural to **1**, as indicated by their powder XRD patterns.

The structures of compounds **1** and **2** are identical to that of $\text{Zn}_2(\text{O}_3\text{PC}_6\text{H}_4\text{PO}_3)(\text{H}_2\text{O})_2$ [9] except some differences in bond lengths and angles [Zn–O 2.009(3)–2.339(4) Å; O–Zn–O 66.3(2)–168.2(2)°]. The structural differences between the title compounds and $\text{Cu}_2(\text{O}_3\text{PC}_6\text{H}_4\text{PO}_3)(\text{H}_2\text{O})_2$ [10], however, are more significant. In compound $\text{Cu}_2(\text{O}_3\text{PC}_6\text{H}_4\text{PO}_3)(\text{H}_2\text{O})_2$, each Cu atom has a distorted square pyramidal coordination environment. Four of its five coordination sites are filled with the phosphonate oxygens, the remaining one by a water molecule. As a result, only one of the three phosphonate oxygens of each {CPO₃} terminus acts as μ_3 -O bridge, leading to an inorganic layer which is different from the one observed in the title compounds.

3.2. Magnetic properties

Figs. 4 and 5 show the temperature dependent molar magnetic susceptibilities of **1** and **2** over the temperature range 2–300 K, measured at 10 kOe. For **1**, the room temperature effective magnetic moment per Co ($4.89 \mu_B$) is much higher than the expected spin only value for spin $S = 3/2$ ($3.87 \mu_B$), which is attributed to the orbital contribution of Co(II) ion. For **2**, the room temperature effective magnetic moment per Ni ($3.04 \mu_B$) is close to the theoretical value for spin $S = 1$ ($2.83 \mu_B$). In both cases, the susceptibility data obey the Curie–Weiss law in the temperature range 50–300 K with Weiss constants –60.5 K for **1** and –28.6 K for **2**, respectively. The continuous decreasing of $\chi_M T$ upon cooling further indicates dominant antiferromagnetic interactions between the magnetic centers in both compounds.

Since both compounds **1** and **2** have pillared layered structures and within the inorganic layer the metal ions

Fig. 4. χ_M and $\chi_M T$ versus T plots for **1**.Fig. 5. χ_M and $\chi_M T$ versus T plots for **2**.

are cross-linked by phosphonate oxygens, their magnetic behaviors may be analyzed in terms of a 2D square-planar Heisenberg model [17]. Theoretical fitting of the χ_M versus T plots based on this model were, however, not successful in both cases. Nevertheless, the position of the maximum (T_{\max}) in the χ_M versus T plot can be related directly to the intraplanar exchange constant J/k by equation: $\tau = kT_{\max}/|J|S(S+1)$ [18]. With regard to compound **2**, T_{\max} is 10.18 K. And for system with $S = 1$, τ is 2.20. Hence the estimated J/k value is -2.3 K. For compound **1**, the T_{\max} appears at ca. 2 K. But similar calculation could not be performed because of the stronger uncertainty concerning the true spin dimensionality of the high-spin Co(II) containing compounds [19].

The magnetic behaviors of various metal phosphonates with similar layered or pillared layered structures have been studied [20,21]. Most of them exhibit characters of 2D antiferromagnetism except a few exceptions such as compound $\text{Cu}_2(\text{H}_2\text{O})_2\{\text{O}_3\text{PCH}_2\text{N}(\text{C}_2\text{H}_4)_2\text{NCH}_2\text{PO}_3\}$ which show ferromagnetic interactions [22]. For those with dominant antiferromagnetic interactions, the intralayer exchange coupling constants (J/k) are found between -1.5 and -5 K [21]. Clearly,

the estimated J value for compound **2** falls in the same order with those 2D compounds. This value is in agreement with those reported earlier for compounds $\text{Ni}(\text{CH}_3\text{PO}_3)(\text{H}_2\text{O})$ ($J/k = -2.7$ K) [23] and $\text{Ni}(\text{RPO}_3)(\text{H}_2\text{O})$ ($J/k = -1.5$ K for $R = \text{CH}_3$, C_2H_5 ; -2.5 K for $R = \text{phenyl}$) [19].

In summary, this paper reports two new metal diphosphonates $\text{Co}_2(\text{O}_3\text{PC}_6\text{H}_4\text{PO}_3)(\text{H}_2\text{O})_2$ (**1**) and $\text{Ni}_2(\text{O}_3\text{PC}_6\text{H}_4\text{PO}_3)(\text{H}_2\text{O})_2$ (**2**) synthesized under hydrothermal condition. The two compounds are isostructural. Both exhibit pillared layered structures built up from inorganic layers and the organic cross-linkages. Antiferromagnetic interactions are found in both cases.

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References

- [1] B. Zhang, A. Clearfield, *J. Am. Chem. Soc.* 119 (1997) 2751.
- [2] G. Alberti, in: J.M. Lehn (Ed.), *Comprehensive Supramolecular Chemistry*, Vol. 7, Pergamon, Elsevier Science Ltd., Oxford, UK, 1996.
- [3] G. Cao, H. Hong, T.E. Mallouk, *Acc. Chem. Res.* 25 (1992) 420.
- [4] C. Maillot, P. Janvier, M. Pipelier, T. Praveen, Y. Andres, B. Bujoli, *Chem. Mater.* 13 (2001) 2879.
- [5] R. Gomez, J.L. Segura, N. Martin, *J. Org. Chem.* 65 (2000) 7566.
- [6] S.B. Ungashe, W.L. Wilson, H.E. Katz, G.R. Scheller, T.M. Putvinski, *J. Am. Chem. Soc.* 114 (1992) 8717.
- [7] G. Cao, H. Lee, V.M. Lynch, T.E. Mallouk, *Inorg. Chem.* 27 (1988) 2781.
- [8] A. Clearfield, in: K.D. Karlin (Ed.), *Progress in Inorganic Chemistry*, Vol. 47, Wiley, New York, 1998, p. 371 and references therein.
- [9] D.M. Poojary, B.L. Zhang, P. Bellinghauson, A. Clearfield, *Inorg. Chem.* 35 (1996) 5254.
- [10] D.M. Poojary, B.L. Zhang, P. Bellinghauson, A. Clearfield, *Inorg. Chem.* 35 (1996) 4942.
- [11] P. Tavs, *Chem. Ber.* 103 (1970) 2428.
- [12] O. Kahn, *Molecular Magnetism*, VCH Publishers, Inc., New York, 1993.
- [13] SAINT, Program for Data Extraction and Reduction, Siemens Analytical X-ray Instruments, Madison, WI, 1994–1996.
- [14] SHELXTL (version 5.0), Reference Manual, Siemens Industrial Automation, Analytical Instruments, Madison, WI, 1995.
- [15] (a) P. Rabu, P. Janvier, B. Bujoli, *J. Mater. Chem.* 9 (1999) 1323.
(b) D.L. Lohse, S.C. Sevov, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 1619;
(c) P. Yin, S. Gao, L.-M. Zheng, Z. Wang, X.-Q. Xin, *Chem. Commun.* (2003) 1076
(d) E.V. Bakhmutova, X. Ouyang, D.G. Medvedev, A. Clearfield, *Inorg. Chem.* 42 (2003) 7046.

- [16] K.J. Martin, P.J. Squattrito, A. Clearfield, *Inorg. Chim. Acta* 155 (1989) 7.
- [17] M.E. Lines, *J. Phys. Chem. Solids* 31 (1970) 101.
- [18] J. DeJongh, A.R. Miedema, *Adv. Phys.* 23 (1974) 1.
- [19] J. LeBideau, C. Payen, B. Bujoli, P. Palvadeau, J. Rouxel, *J. Magn. Magn. Mater.* 140–144 (1995) 1719.
- [20] S.G. Carling, P. Day, D. Visser, R.K. Kremer, *J. Solid State Chem.* 106 (1993) 111.
- [21] C. Bellitto, in: J.S. Miller, M. Drillon (Eds.), *Magnetism: Molecules to Materials II: Molecule-Based Materials*, Wiley-VCH Verlag GmbH & Co. KGaA, New York, 2002, p. 425 and references therein.
- [22] Y. Wang, S.-S. Bao, W. Xu, J. Chen, S. Gao, L.-M. Zheng, *J. Solid State Chem.* 177 (2004) 1297.
- [23] C. Bellitto, E.M. Bauer, S.A. Ibrahim, M.R. Mahmoud, G. Righini, *Chem. Eur. J.* 9 (2003) 1324.