

Cobalt Borate Phosphate, $\text{Co}_3[\text{BPO}_7]$, Synthesis and Characterization

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Single crystals of $\text{Co}_3[\text{BPO}_7]$ were obtained by boron flux method and characterized by single-crystal diffraction data. The compound crystallizes in the monoclinic space group Cm with $a = 9.774(2)$, $b = 12.688(2)$, $c = 4.9057(8)$ Å, $\beta = 119.749(2)^\circ$; $V = 528.20(15)$ Å³; $Z = 4$. The structure consists of Co in trigonal bipyramids, square pyramids, and distorted octahedra. Polyhedral Co centers, triangular B centers, and tetrahedral P centers are joined together to form a three-dimensional network. The temperature dependence of the magnetic susceptibility of the compound follows the Curie–Weiss law to 30 K. Below this temperature, the magnetic behavior displayed first antiferromagnetic ordering followed by ferrimagnetic coupling at 25 K. © 2001 Academic Press

Key Words: cobalt borate–phosphate; crystal structure; magnetic properties.

INTRODUCTION

Borate and phosphate compounds have been a topic of interest due to their magnetic, optical, and electrooptical applications (1–3). The diversity in the linkage of boron and phosphorus atoms with oxygen has led to the preparation of new compounds with different anionic partial structures (4). Although most of the borophosphate compounds were obtained hydrothermally, the high-temperature syntheses method (heating of solid mixtures in the open air system) has produced anhydrous borophosphates, which are the followings: $M[\text{BPO}_5]$ ($M = \text{Ca}, \text{Sr}$), $M_3[\text{BP}_3\text{O}_{12}]$ ($M = \text{Ba}, \text{Pb}$) and $\text{Na}_5[\text{B}_2\text{P}_3\text{O}_{13}]$ (5–7). The primary building units of these chain structures are BO_4 and PO_4 corner-sharing tetrahedra. Trigonal planar groups sharing one oxygen atom with a phosphate tetrahedron and isolated phosphate tetrahedra are present in the crystal structure of $\text{Co}_5[\text{BP}_3\text{O}_{14}]$ (8), which was also obtained by the high-temperature boron flux method.

The isostructural compounds $\text{Zn}_3[\text{BPO}_7]$ and $\text{Mg}_3[\text{BPO}_7]$ (9–12) contain isolated planar BO_3 groups and

PO_4 tetrahedra and are classified as borate–phosphates. Liebertz *et al.*, reported that compounds $\text{Zn}_3[\text{BPO}_7]$ and $\text{Mg}_3[\text{BPO}_7]$ both occur in two forms; one is orthorhombic with probable space group $Imm2$ at low temperatures and the other is hexagonal with the space group $P6m2$ or $P62m$ at high temperatures.

The phosphates such as KTiOPO_4 or borates such as BaB_2O_4 have been widely used in electrooptical applications such as frequency conversions in laser spectroscopy. It is expected that the combination of the phosphate group and the borate group in the same crystalline materials may generate a whole new class of materials with novel properties. Until now, there have been very few materials that contain both phosphate and borate groups. Another stimulus for the study of cobalt borate and phosphate is the interesting magnetic properties that they may possess and the sensitivity of their magnetic properties to the coordination environment (13). NaCoPO_4 has linear Curie–Weiss behavior until 12 K, and below this temperature it shows ferromagnetic ordering (14). Carling *et al.* worked on the magnetic ordering of $M^I\text{CoPO}_4 \cdot \text{D}_2\text{O}$ ($M^I = \text{K}, \text{NH}_4$) and found that it was very weak, although it is clear that the magnetic and chemical unit cells are not coincident (15). $\text{Co}_{0.5}\text{Ti}(\text{PO}_4)$ belongs to the Nasicon-type family and has a typical paramagnetic behavior of an isolated Co^{+2} ions located in a distorted octahedral site (16). In the magnetic properties of borate compounds, iron borate FeBO_3 is classified as weakly ferromagnetic with magnetic anisotropy of easy plane type (17) and Fe is dispersed in aluminum borate to obtain a magnetically interesting nanocomposite (18). Norrestam *et al.*, worked on the $\text{SrCu}_2(\text{BO}_3)_2$ system, the measured magnetic susceptibilities of which indicate a transition to an antiferromagnetic state below 14 K (19). The magnetic susceptibility study of borophosphate compounds is very rare. Recently, Bontchev *et al.*, synthesized vanadium borophosphate cluster anions with piperazine, ammonium, and alkali metals. Below 120 K, the magnetic properties are dominated by antiferromagnetic interaction in isolated V dimers (20).

In this report, we will describe the synthesis and characterization of a new cobalt borophosphate with PO_4 and

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isolated planar BO_3 groups. The title compound has monoclinic crystal structure with Cm space group.

EXPERIMENTAL

Synthesis

The title compound was made in a flux of H_3BO_3 (five fold excess) from a stoichiometric mixture of $\text{CoCO}_3 \cdot x\text{H}_2\text{O}$ (Aldrich) and $\text{NH}_4\text{H}_2\text{PO}_4$ (Fisher 99%). The mixture was calcined at 400°C for 4 h and ground well before heating at 1050°C for 3 h. The heated sample was subsequently cooled to 600°C for a period of 6 h and then cooled to room temperature. The reaction product was washed with distilled water several times to remove excess boron. The crystals were platelike and purple colored.

Single-Crystal Analysis

A crystal was glued to a thin glass fiber with epoxy resin and mounted on a Bruker Smart CCD diffractometer equipped with a normal focus, 2.4-kW sealed tube X-ray source ($\text{MoK}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$) operating at 45 kW and 40 mA. Room temperature intensity data were collected with scans (width of 0.30 \AA and exposure time of 0.30 s per frame). The empirical absorption corrections were based on the equivalent reflections, and other possible effects such as absorption by the glass fiber were simultaneously corrected. The structure was solved by direct methods followed by successive difference Fourier methods. All calculations were performed using SHELXTL running on Silicon Graphics Indy 5000. Final full-matrix refinements were against F^2 and the crystallographic results are summarized in Table 1. After the refinement, the structure

was examined for additional symmetry elements using the program PLATON and none were detected.

Magnetic Susceptibility

Susceptibility measurements were carried out using Quantum Design MPMS-5S Magnetic Properties Measuring System. Data were collected over the temperature range of 2–300 K with an applied field of 50 G in zero-field cooling and field cooling region.

Thermal Analyses

The stability of the title compound to heat was analyzed with thermogravimetric analysis (TG) and differential thermal analysis (DTA), which were performed on a Netzsch Simultaneous Thermal Analysis (STA) 409 system in static air with a heating rate of $5^\circ\text{C}/\text{min}$ from 30 to 1100°C using a sample weight of 50.0 mg. No weight loss was observed in TG as expected. There was one endothermic peak around 1050°C .

RESULTS AND DISCUSSION

Crystal Structure

There are three unique Co sites, two unique P sites, and one unique B site (Fig. 1 and Table 2). All three Co sites have distinct coordination environments. The Co1 site adopts a trigonal bipyramidal coordination with Co–O distance ranging from 1.992 to 2.084 \AA (the sixth closest oxygen atom is 2.894 \AA away). The Co2 site has square pyramidal coordination with a Co–O distance ranging from 2.033 to 2.107 \AA (Table 3, the sixth closest oxygen atom is 2.721 \AA away). The Co3 site has a distorted octahedral environment with

TABLE 1
A Summary of Crystal Data and Refinement Results

Name	Cobalt borate phosphate
Formula	$\text{Co}_3[\text{BPO}_7]$
Size (μm)	$160 \times 133 \times 40$
a	$9.774(2) \text{ \AA}$
b	$12.688(2) \text{ \AA}$
c	$4.9057(8) \text{ \AA}$
β ($^\circ$)	$119.749(2)$
V (\AA^3)	$528.20(15)$
Z	4
Space group	Cm
$2\theta_{\text{max}}$ (deg)	56
Total data	2719
Unique data	1219
Data, $I > \sigma_2(I)$	1192
Parameters	120
$R(F)$ (%)	4.93
$R_w(F^2)$ (%)	13.9
GOF	1.87

Note. $R(F) = [\sum ||F_o| - |F_c||] / \sum |F_o|$ with $F_o > 4.0 \sigma(F)$.

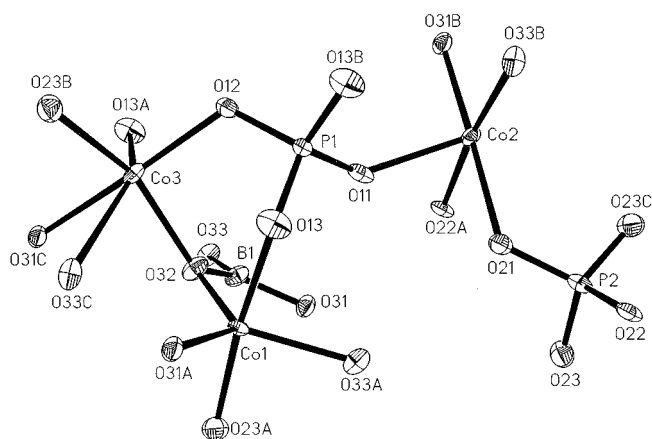


FIG. 1. The ORTEP view of coordination environments for Co, B, and P atoms in the asymmetric unit. Atom labels having "A," "B," or "C" refer to symmetry-generated atoms.

TABLE 2
Atomic Coordinates ($\times 10^{-4}$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for Co₃[BPO₇]

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Co(1)	− 5965(2)	− 2500(1)	− 2035(4)	9(1)
Co(2)	− 4151(2)	− 1124(1)	− 5189(3)	12(1)
Co(3)	− 9250(2)	− 1384(1)	− 5666(3)	14(1)
B(1)	− 12663(16)	− 2192(12)	− 8679(32)	17(3)
P(1)	− 618(5)	0	− 2298(10)	13(1)
P(2)	− 5991(6)	0	− 2091(12)	15(1)
O(11)	− 2403(13)	0	− 4381(25)	16(2)
O(12)	− 9781(12)	0	− 4306(29)	22(3)
O(13)	− 117(10)	1004(7)	− 239(19)	23(2)
O(21)	− 4554(13)	0	− 2540(25)	16(2)
O(22)	− 5526(13)	0	1449(26)	17(2)
O(23)	− 6941(10)	1013(6)	− 3615(20)	21(2)
O(31)	− 3906(9)	− 2136(6)	1870(19)	16(2)
O(32)	− 11137(9)	− 2234(6)	− 6196(19)	18(2)
O(33)	− 7954(10)	− 2771(7)	− 1738(18)	17(2)

Note. *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

a Co–O distance ranging from 2.018 to 2.448 Å (the seventh oxygen atom is 3.206 Å away). Polyhedral Co centers, triangular B centers, and tetrahedral P centers are joined together to form a three-dimensional network (Fig. 2). In fact, because of the high Co concentration in the title compound, there is a three-dimensional network of Co–O link-

ages, in which polyhedral Co centers are connected by a combination of edge- and corner-sharing. Such a feature may be more relevant to the magnetic properties of the title compound.

The B site has regular trigonal planar coordination, which distinguishes the title compound from a related cobalt borophosphate, CoB₂P₃O₁₂(OH)C₂H₁₀N₂, in which the B site adopts the tetrahedral coordination (21). Both tetrahedral P sites are located on the crystallographic mirror planes. It is worth noting that the title compound does not contain B–O–P linkages. Such a feature distinguishes the title compound from other known borophosphates such as Co₅[BP₃O₁₄] (8). The triangular B sites and tetrahedral P sites are connected to Co polyhedral centers by corner-sharing of oxygen atoms. Of nine unique oxygen atom sites, phosphate oxygen atoms (O11 through O13 and O21 through O23) are coordinated between two Co centers and one P center. On the other hand, two of the borate oxygen atoms (O31 and O33) are surrounded by three Co centers (the Co–O distance ranges from 2.026 to 2.346 Å for O31 and 2.049 to 2.448 Å for O33), whereas the O32 site is coordinated to two Co sites (the third closest Co site is 2.721 Å away).

Magnetic Susceptibility Measurement

Figure 3 shows the temperature dependence of the magnetic susceptibility and reciprocal susceptibility for the

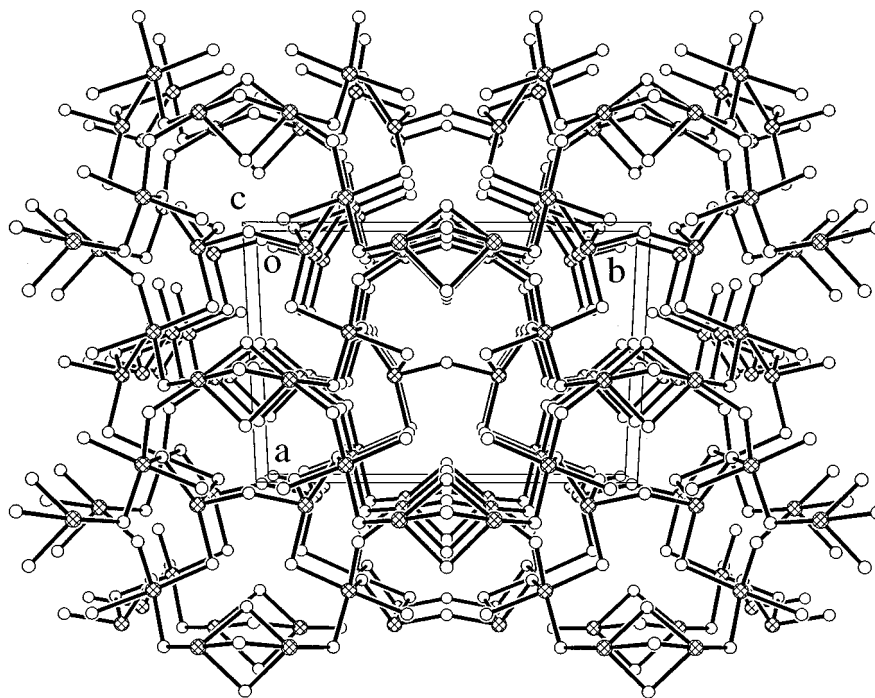


FIG. 2. The projection of a three-dimensional network of Co–O linkages down the unit cell *c* axis.

TABLE 3
Selected Bond Lengths (Å) and Angles (°) for Co₃[BPO₇]

Co(1)–O(32) 1.992(8)	
Co(1)–O(31) 2.026(8)	B(1)–O(31) 1.37(2)
Co(1)–O(33) 2.049(8)	B(1)–O(32) 1.38(2)
Co(1)–O(23) 2.082(8)	B(1)–O(33) 1.38(2)
Co(1)–O(13) 2.084(8)	
Co(2)–O(31) 2.033(8)	P(1)–O(11) 1.522(11)
Co(2)–O(33) 2.058(8)	P(1)–O(13) 1.547(9)
Co(2)–O(22) 2.088(8)	P(1)–O(12) 1.562(13)
Co(2)–O(21) 2.094(8)	
Co(2)–O(11) 2.107(8)	
Co(3)–O(23) 2.018(8)	O(31)–Co(2)–O(33) 86.2(3)
Co(3)–O(13) 2.024(9)	O(31)–Co(2)–O(22) 97.3(3)
Co(3)–O(32) 2.039(8)	O(33)–Co(2)–O(21) 174.6(4)
Co(3)–O(31) 2.346(8)	O(33)–Co(2)–O(21) 99.1(3)
Co(3)–O(33) 2.448(8)	O(22)–Co(2)–O(21) 77.3(3)
O(32)–Co(1)–O(31) 123.1(3)	
O(32)–Co(1)–O(33) 116.3(3)	O(31)–B(1)–O(32) 120.2(11)
O(31)–Co(1)–O(33) 120.2(3)	O(31)–B(1)–O(33) 119.4(11)
O(23)–Co(1)–O(13) 174.5(4)	O(32)–B(1)–O(33) 120.4(11)
O(23)–Co(3)–O(13) 104.3(4)	
O(23)–Co(3)–O(32) 154.7(3)	
O(12)–Co(3)–O(31) 169.9(4)	
O(11)–P(1)–O(13) 108.9(4)	
O(13)–P(1)–O(12) 108.5(4)	
O(13)–P(1)–O(13) 110.9(7)	

Note. Symmetry transformations used to generate equivalent atoms: $x, y, z; x, -y, z; x + \frac{1}{2}, y + \frac{1}{2}, z; x + \frac{1}{2}, -y + \frac{1}{2}, z$. Estimated standard deviations are in parentheses.

Co₃[BPO₇] compound. The data indicate that the compound has paramagnetic Curie–Weiss behavior in the temperature range 30–300 K. The bond valence sum calculations confirmed the charge of +2 for cobalt. The effective magnetic moment for 3Co, calculated from the

derived Curie constant, is $4.74 \mu_B$. This value indicates the spin state of Co⁺² as low spin ($d^7, S = 1/2$). The extrapolated Weiss constant has a negative value of -35 K. The negative Weiss constant implies that the superexchange interactions between neighboring Co atoms, i.e., Co(1)–O(3)–Co(2) units, are very weak and antiferromagnetic in character. There is a little upturn in the magnetic susceptibility between 25 and 30 K. It appears that Co atoms begin to order antiferromagnetically at 30 K and exhibit a canted antiferromagnetic behavior that changes to ferromagnetic coupling at 25 K. In the temperature range below 10 K, Co₃[BPO₇] shows a ferromagnetic ordering (i.e., an increase in magnetization at low temperatures).

CONCLUSION

The title compound was synthesized by the boron flux method. The crystal structure analysis shows that polyhedral Co centers, triangular B centers, and tetrahedral P centers are joined to form a three-dimensional network. The effective magnetic moment derived from magnetic susceptibility and bond valence sum calculations confirmed the low spin Co⁺² ion. Magnetic susceptibility versus temperature measurement indicates that the compound has ferromagnetic behavior at low temperatures, followed by antiferromagnetic and then paramagnetic behavior with increasing temperature (22–24).

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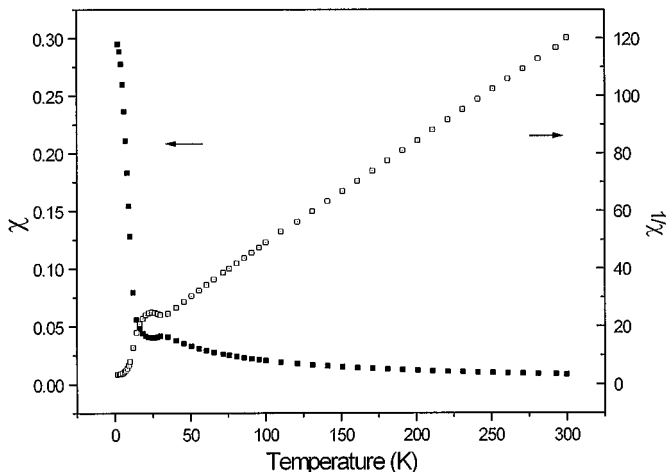


FIG. 3. Temperature dependence of the magnetic susceptibility and inverse susceptibility vs temperature (K) for Co₃[BPO₇].

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