

# Synthesis, Crystal Structure, and Magnetic and Electric Properties of the Cross-Linked Chain Cobalt Oxychloride $\text{Ba}_5\text{Co}_5\text{ClO}_{13}$

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The cross-linked chain cobalt oxychloride  $\text{Ba}_5\text{Co}_5\text{ClO}_{13}$  is reported. Single crystals were obtained by a flux method with  $\text{BaCl}_2$ . A hexagonal unit cell ( $P6_3/mmc$ ,  $a = 5.6980(8) \text{ \AA}$  and  $c = 24.469(5) \text{ \AA}$ ) was found. The +3 and +4 valence cobalt ions were formally distributed into octahedral and tetrahedral sites coordinated by oxide ions. The compound was electrically insulating with a gap of 0.25 eV along the chain. Antiferromagnetism was found, with substantial ferromagnetic character, suggesting that the magnetic ground state is complex. © 2001 Academic Press

## I. INTRODUCTION

In the past few decades, the understanding of the electronic properties of transition metal compounds has advanced steadily (1). Unusual electronic properties, such as colossal magnetoresistivity, spin-triplet superconductivity, and high- $T_c$  superconductivity, are of particular current interest. We have recently been studying cobalt-based compounds in order to find additional systems showing correlations among their magnetic and electronic transport properties and crystal structures.

Here we report the cobalt oxychloride  $\text{Ba}_5\text{Co}_5\text{ClO}_{13}$ , recently discovered when synthesis conditions for growing crystals of  $\text{BaCoO}_3$  by means of a flux method with  $\text{BaCl}_2$  (2–5) were being explored. The crystal growth was followed by studies of crystal structure, electronic transport, and magnetic properties of the crystals. The compound was found to be an oxychloride and isostructural to  $\text{Ba}_{10}\text{Fe}_8\text{Pt}_2\text{Cl}_2\text{O}_{25}$  ( $P6_3/mmc$ ,  $a = 5.8034(4) \text{ \AA}$  and  $c = 24.997(5) \text{ \AA}$ ), which has a cross-linked chain structure (6). The crystal structure of the cobalt oxychloride is related to that of the quasi-one-dimensional cobalt oxide  $\text{BaCoO}_3$  ( $P6_3/mmc$ ,  $a = 5.650(1) \text{ \AA}$  and  $c = 4.748(1) \text{ \AA}$ ), which consists

of face-shared  $\text{CoO}_6$  chains and Ba insertions (3). The chains are disconnected in the cobalt oxychloride after three  $\text{CoO}_6$  face-shared octahedra by interchain tetrahedral  $\text{CoO}_4$  units and the Ba–Cl network. The compound is electrically resistive along the broken chain. In the cobalt oxychloride, both antiferromagnetic and ferromagnetic components coexist and the magnetic ground state is complex, as in the quasi-one-dimensional compound  $\text{BaCoO}_3$  (3–5).

## II. EXPERIMENTAL AND SAMPLE CHARACTERIZATION

The crystals of  $\text{Ba}_5\text{Co}_5\text{ClO}_{13}$  were grown as follows. A 6-g mixture of  $\text{BaCO}_3$ ,  $\text{Co}_3\text{O}_4$ , and  $\text{BaCl}_2$  with the ratio 1:  $\frac{1}{3}$ : 2, respectively, was placed into a covered alumina crucible (cylindrical, 22 mm  $\phi \times$  33 mm) and then heated at 1000°C in air for 3 h. The heating was followed by cooling at 0.5°C/min to 850°C and quenching in air at room temperature. Crystals were separated from the flux by brief treatment in a sonic bath consisting of an approximately 5:1 mixture of methanol with water. Shiny, black crystals up to 0.8 mm in largest dimension were obtained.

A selected crystal was mounted on a glass fiber in a four-circle X-ray diffractometer. An almost full sphere of the diffraction data was collected on a Bruker AXS Smart CCD area detector system with graphite-monochromatized  $\text{MoK}\alpha$  radiation. The data were indexed on a twin structure model consisting of two components of approximately equal volume. Orientation of the components is related with a 178.5° rotation around the hexagonal [010] axis. Both sets of spots were integrated using the twinsolve software (7). Using nonoverlapping reflections from the major component, an incident/diffracted beam correction was applied (7);  $R_{\text{int}}$  decreased from 0.150 to 0.075 with reflections at  $I > 5\sigma(I)$ . After rejection of systematic absences and outliers, there remained 4386 reflections at  $R_{\text{int}} = 0.065$ , giving 434 independent reflections out of 439 available within 60° in diffraction angle. Finally, the radius of an equivalent

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sphere was estimated as Blessing described (8), and the ABSORB routine from the NRCVAX package was applied to correct a spherical absorption (9). All subsequent calculations were carried out with the NRCVAX suite of programs (9).

The magnetic and electrical properties of the crystals were studied by a commercial apparatus (PPMS, Quantum Design) between 5 and 400 K. The highest applied magnetic field was 90 kOe. A conventional four-probe ac technique was employed for the electrical resistivity measurement. The Seebeck coefficient was measured in a commercial apparatus (Seebeck Measurement System, MMR Technologies) between 114 and 174 K.

### III. RESULTS AND DISCUSSIONS

The crystallographic data for  $\text{Ba}_5\text{Co}_5\text{ClO}_{13}$  are summarized in Tables 1 and 2, and selected bond distances and angles are in Table 3. In Fig. 1, a view of the structure of  $\text{Ba}_5\text{Co}_5\text{ClO}_{13}$  is presented, based on the final structure parameters (Tables 1 and 2). It is isostructural to  $\text{Ba}_{10}\text{Fe}_8\text{Pt}_2\text{Cl}_2\text{O}_{25}$  (6). These compounds have a characteristic lattice in which two kinds of anion are mixed, while transition metals are coordinated only by oxide ions. The chloride ion is coordinated by five Ba ions, two Ba(2) ions at 2.962(2) Å, and three Ba(3) ions at 3.290(1) Å, forming a trigonal bipyramid (Fig. 2). Interestingly, the chloride ions are well shielded from oxide ions by forming the bipyramids. The cobalt ions are found in two coordinate forms, octahedral and tetrahedral. Three  $\text{CoO}_6$  octahedra are connected by sharing those faces, resulting in short Co to Co distances of 2.518(3) Å. The blocks of three  $\text{CoO}_6$  octahedra are connected to  $\text{Co}_2\text{O}_7$  tetrahedral units at each corner. The

**TABLE 2**  
Atomic Coordinates and Isotropic Atomic Displacement Parameters at 23°C for  $\text{Ba}_5\text{Co}_5\text{ClO}_{13}$

Atom	Position	Occupancy	x	y	z	$B_{\text{iso}}$ (Å <sup>2</sup> )
Ba(1)	2b	1	0	0	$\frac{1}{4}$	1.14(4)
Ba(2)	4f	1	$\frac{1}{3}$	$\frac{2}{3}$	0.371 04(6)	0.56(3)
Ba(3)	4f	1	$\frac{1}{3}$	$\frac{2}{3}$	0.959 97(5)	0.61(4)
Co(1)	4e	1	0	0	0.602 86(11)	0.37(8)
Co(2)	4f	1	$\frac{1}{3}$	$\frac{2}{3}$	0.823 29(12)	0.55(8)
Co(3)	2a	1	0	0	0	0.42(8)
Cl	2c	1	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	1.95(20)
O(1)	12k	1	0.839(1)	0.161 <sup>a</sup>	0.3504(3)	0.83(14)
O(2)	12k	1	0.146(1)	0.854 <sup>a</sup>	0.4492(3)	0.64(14)
O(3)	2d	1	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{3}{4}$	2.8(7)

<sup>a</sup>1 - x.

tetrahedra are sharing O(3). The Ba ions are distributed into three crystallographic sites: Ba(1) is coordinated by six oxide ions at 2.926(7) Å and three oxide and three chloride ions at 3.290(1) Å (Fig. 3a). Ba(2) is also coordinated by both oxide and chloride ions; three oxide ions at 2.660(7) Å, six oxide ions at 2.894(6) Å, and a chloride ion at 2.962(2) Å (Fig. 3b). Ba(3) shows an oxygen only coordination with distances of 2.868(6) Å (×6), 2.891(7) Å (×3), and 3.175(8) Å (×3) (Fig. 3c). It should be noted that the Ba(1), Cl, and O(3) are all coplanar at  $z = \frac{1}{4}$  and  $\frac{3}{4}$  with the six coplanar ions around Ba(1) symmetrically arranged (Fig. 3a).

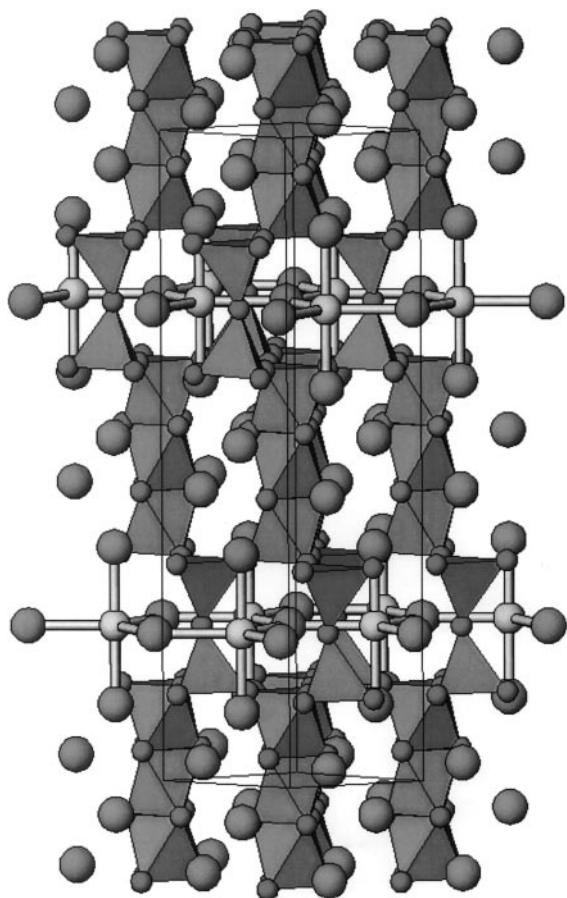
In the course of the crystallographic study, oxygen and chlorine nonstoichiometry were investigated. Although

**TABLE 1**  
Crystallographic Data at 23°C for  $\text{Ba}_5\text{Co}_5\text{ClO}_{13}$

Space group	$P6_3/mmc$ (No. 194)
Crystal size (mm)	$0.1 \times 0.4 \times 0.4$
$a$ (Å)	5.6980(8)
$c$ (Å)	24.469(5)
$V$ (Å <sup>3</sup> )	688.0(2)
$Z$	2
Absorption correction	Spherical (radius 0.15 mm)
$\mu$ (MoK $\alpha$ , mm <sup>-1</sup> )	20.17
Minimum transmission	0.12621
Maximum transmission	0.153119
Radiation	MoK $\alpha$
Scan type	$\Omega$
Reflection measured	4684
Independent reflections	434
Observed reflections ( $I > 2.5\sigma(I)$ )	342
Refined parameters	27
$R_t$	0.022
$R_w$ ( $W = 1/\sigma^2(F_o)$ )	0.042
Extinction length ( $\mu\text{m}$ )	0.2634

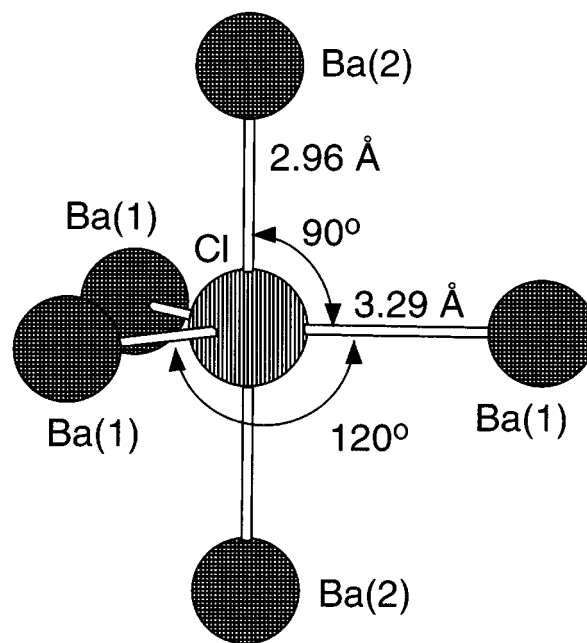
**TABLE 3**  
Selected Interatomic Distances and Angles at 23°C for  $\text{Ba}_5\text{Co}_5\text{ClO}_{13}$

Atoms	Distance (Å)	Atoms	Distance (Å)
Co(1)–O(1)	1.958(6) × 3	Ba(2)–O(1)	2.894(6) × 6
Co(1)–O(2)	1.923(7) × 3	Ba(2)–O(2)	2.660(7) × 3
Co(2)–O(1)	1.826(4) × 3	Ba(2)–Cl	2.962(2) × 1
Co(2)–O(3)	1.793(3) × 1	Ba(3)–O(1)	3.175(8) × 3
Co(3)–O(2)	1.903(5) × 6	Ba(3)–O(2)	2.868(6) × 6
Ba(1)–O(1)	2.926(7) × 6	Ba(3)–O(3)	2.891(7) × 3
Ba(1)–O(3)	3.290(1) × 3	Co(1)–Co(3)	2.518(3)
Ba(1)–Cl	3.290(1) × 3		
Atoms	Angle (degree)	Atoms	Angle (degree)
O(1)–Co(1)–O(1)	89.3(4)	O(2)–Co(3)–O(2)	82.0(3)
O(1)–Co(1)–O(2)	94.8(4)	O(2)–Co(3)–O(2)	98.1(3)
O(1)–Co(1)–O(2)	174.3(75)	O(2)–Co(3)–O(2)	180
O(2)–Co(1)–O(2)	80.9(5)	Co(1)–O(1)–Co(2)	165.6(29)
O(1)–Co(2)–O(1)	107.6(4)	Co(1)–O(2)–Co(3)	82.3(4)
O(1)–Co(2)–O(3)	111.3(5)	Co(2)–O(3)–Co(2)	180



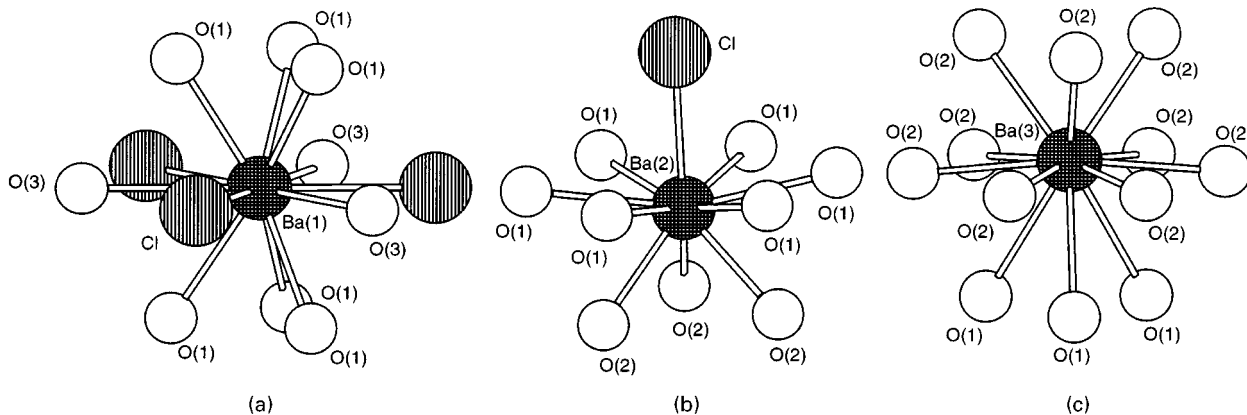
**FIG. 1.** Schematic crystal structure view for  $\text{Ba}_5\text{Co}_5\text{ClO}_{13}$ . The hexagonal unit cell ( $P6_3/mmc$ ;  $a = 5.6980(8) \text{ \AA}$  and  $c = 24.469(5) \text{ \AA}$ ) is indicated by solid lines. The large, small, and light gray spheres represent barium, oxygen, and chlorine atoms, respectively. The  $\text{CoO}_6$  octahedra and  $\text{CoO}_4$  tetrahedra are shown as ms polyhedra.

$\text{Ba}(2)$  is under compression with a calculated valence approaching 3, indicating a possibility of vacancies at the  $\text{O}(2)$  site (closest to  $\text{Ba}(2)$  at  $2.660(7) \text{ \AA}$ ), the oxygen site  $\text{O}(2)$  is

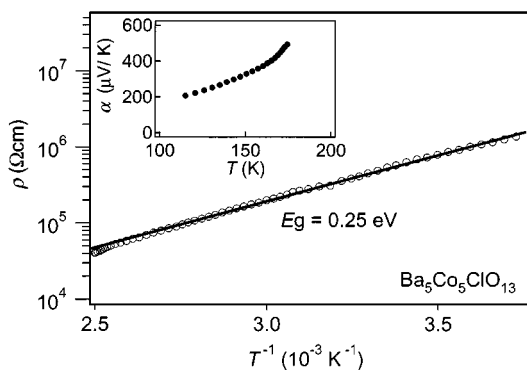


**FIG. 2.** Schematic view of the  $\text{Ba}_5\text{Cl}$  polyhedron of  $\text{Ba}_5\text{Co}_5\text{ClO}_{13}$ . The linear  $\text{Ba}(2)\text{-Cl-Ba}(2)$  bond is along the  $c$  axis.

fully occupied. Despite the larger isotropic atomic displacement parameter at the  $\text{O}(3)$  site, the  $\text{Co}_2\text{O}_7$  unit has fully occupied oxygen sites in contrast to  $\text{Ba}_{10}\text{Fe}_8\text{Pt}_2\text{Cl}_2\text{O}_{25}$ , where the corner-shared oxygen ( $\text{O}(3)$ ) is only half occupied (6). The isotropic atomic displacement parameters of the plane coordinated  $\text{Ba}(1)$  and  $\text{Cl}$  (Fig. 2) are slightly larger than conceivable level. These facts indicate the possibility of nonstoichiometry or structural anomaly in the  $\text{Ba-Cl}$  plane, even though insignificant vacancies were suggested at the  $\text{Cl}$  site by the parameter refinements. Further microscopic studies on the structure could help to figure out the issue. The composition of the cobalt oxychloride is rather stoichiometric  $\text{Ba}_5\text{Co}_5\text{ClO}_{13}$  in agreement with the ideal composition. The possibility that all oxygen sites having

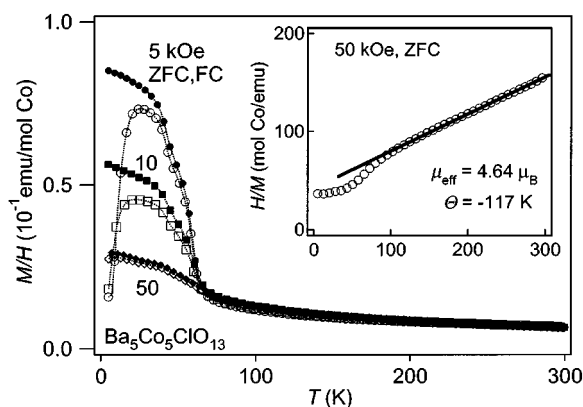


**FIG. 3.** Schematic views for the barium oxychloride and oxide polyhedra of  $\text{Ba}_5\text{Co}_5\text{ClO}_{13}$ . (a)  $\text{BaCl}_3\text{O}_9$ , (b)  $\text{BaClO}_9$ , and (c)  $\text{BaO}_{12}$ .

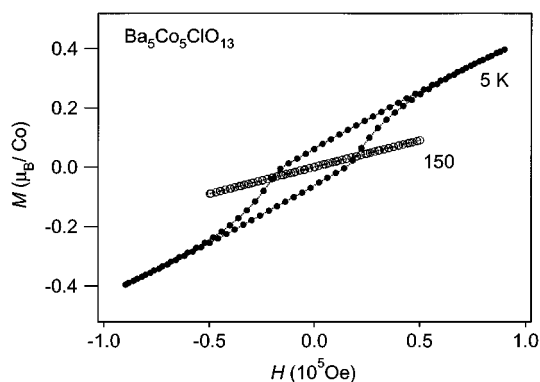


**FIG. 4.** Temperature dependence of the resistivity of the crystal  $\text{Ba}_5\text{Co}_5\text{ClO}_{13}$ . A plot of  $\log \rho$  vs  $T^{-1}$  is shown. The ac current flow is almost parallel to the cross-linked chains. The fit to the linear part, as indicated by the solid line, yields a gap of 0.25 eV. (Inset) Temperature dependence of the thermoelectric coefficient of  $\text{Ba}_5\text{Co}_5\text{ClO}_{13}$ .

a reduced site occupancy could not unambiguously be ruled out, though a statistical reduction of the occupancy factor over all oxygen sites was tested and found not to improve the refinements. The composition  $\text{Ba}_5\text{Co}_5\text{ClO}_{13}$  yields an average Co valence of +3.4, indicating the presence of  $\text{Co}^{4+}$  (or ligand holes at  $\text{Co}^{3+}$ ). A hypothetical composition with a charge-ordered site preference model for the Co ions,  $\text{Co}^{3+}$  for the octahedral sites (Co(1) and Co(2)) and  $\text{Co}^{4+}$  for the tetrahedral site (Co(3)),  $\text{Ba}_{10}\text{Co}_8^{3+}\text{Co}_2^{4+}\text{Cl}_2\text{O}_z$ , does not explain the observed oxygen stoichiometry. The Co ions are, therefore, mixed formally in the tetrahedral and octahedral sites.



**FIG. 5.** Temperature dependence of the magnetic susceptibility of  $\text{Ba}_5\text{Co}_5\text{ClO}_{13}$ , measured at 5, 10, and 50 kOe on heating after cooling the sample without an applied magnetic field (zero field cooling, ZFC (open markers)) and then on cooling in the field (field cooling, FC (solid markers)). The sample consists of the randomly oriented crystals. The inverse magnetic susceptibility is shown in the inset. The Curie-Weiss law fit to the linear part is indicated by the solid line.



**FIG. 6.** The magnetic field dependence of the magnetization of  $\text{Ba}_5\text{Co}_5\text{ClO}_{13}$  at 5 and 150 K. The sample consists of randomly oriented crystals.

The electrical resistivity data are shown in Fig. 4. The resistivity of  $\text{Ba}_5\text{Co}_5\text{ClO}_{13}$  is high ( $E_g = 0.25$  eV). Crystals mechanically separated from the flux using neither water nor methanol were also measured: No significant difference was detected. The thermoelectric coefficient in the studied temperature range is positive (inset in Fig. 4), indicating that p-type electrical carriers are dominant in  $\text{Ba}_5\text{Co}_5\text{ClO}_{13}$ . Due to the highly electrically resistive character of the material it was not possible to obtain the data over a very wide temperature range. Further investigation by spin-polarized band structure calculations could help to explain the observed insulating properties.

The temperature dependence of the magnetic susceptibility of  $\text{Ba}_5\text{Co}_5\text{ClO}_{13}$  was measured at magnetic fields of 5, 10, and 50 kOe on zero field cooling and field cooling. The data are presented in Fig. 5 as  $M/H$  vs  $T$  and  $H/M$  vs  $T$  plots. The data for the magnetic field dependence of the magnetization at 5 and 150 K are shown in Fig. 6. In the higher temperature region, above approximately 130 K, the inverse magnetic susceptibility is linearly dependent on temperature, and the Curie-Weiss law was employed to analyze the linear part. A fit to the CW law yields an effective magnetic moment of  $4.64 \mu_B$  per Co, and a Weiss temperature of  $-117$  K, characteristic of antiferromagnetic interactions. Below approximately 60 K, a change in slope of the  $H/M$  vs  $T$  curve was observed. The magnetic field dependence of the magnetization at 5 K (Fig. 6) reveals the presence of ferromagnetism as seen by the fact that the extrapolation of  $M$  to  $H = 0$  is not zero (the spontaneous magnetization at 5 K is  $\sim 0.08 \mu_B$  per Co). The changes in slope suggest that ferromagnetic interactions are becoming significant below  $\sim 60$  K. Thermomagnetic hysteresis was observed at low temperature for  $\text{Ba}_5\text{Co}_5\text{ClO}_{13}$ . Due to the geometrical configuration of the octahedral and tetrahedral blocks and the mixed valence state of the cobalt ions, the magnetic ground state of  $\text{Ba}_5\text{Co}_5\text{ClO}_{13}$  is complex (10).

As  $\text{Ba}_5\text{Co}_5\text{ClO}_{13}$  is electrically insulating, the observed effective magnetic moment of  $4.64 \mu_B$  per Co is expected to be the average of those of localized  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$  present in the ratio 3:2. Three kinds of  $3d^6$  electron configurations are possible in the octahedral environment for  $\text{Co}^{3+}$  (i.e.,  $t_{2g}^6 e_g^0$ ,  $S = 0$ ;  $t_{2g}^5 e_g^1$ ,  $S = 1$ ;  $t_{2g}^4 e_g^2$ ,  $S = 2$ ), and three kinds of  $3d^5$  (or corresponding  $3d^6 \underline{L}$ ) states for  $\text{Co}^{4+}$  ( $t_{2g}^5 e_g^0$ ,  $S = \frac{1}{2}$ ;  $t_{2g}^4 e_g^1$ ,  $S = \frac{3}{2}$ ;  $t_{2g}^3 e_g^2$ ,  $S = \frac{5}{2}$ ). The cobalt ions are distributed into three sites, two octahedral sites and one tetrahedral site. The present magnetic study, which is a site average of the magnetism, is insufficient to determine the exact electronic configurations of the cobalt ions. Further investigations employing probes more sensitive to the microscopic magnetic environment of different Co sites, such as NMR or Mössbauer effect studies, would be of interest. As in  $\text{BaCoO}_3$ , the related compound  $\text{Ba}_5\text{Co}_5\text{ClO}_{13}$  shows semiconducting character despite non-integer formal Co valence and a complex magnetic state at low temperature involving both antiferromagnetism and ferromagnetism. Consideration of the electronic structure of Co-based chain compounds from a theoretical viewpoint would be of significant interest.

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