Anomalous low-temperature behavior of the Co dimers in the oxo-halide $CoSb_2O_3Br_2$

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ABSTRACT

We report the synthesis, crystal structure determination, magnetic and low-temperature structural properties of a new cobalt antimony oxo-bromide. $CoSb_2O_3Br_2$ crystallizes in the triclinic crystal system, space group $P-1$, with the following lattice parameters: $a = 5.306(3)$ Å, $b = 7.812(4)$ Å, $c = 8.0626(10)$ Å, $\alpha = 88.54(3)°$, $\beta = 82.17(3)°$, $\gamma = 80.32(4)°$, and $Z = 2$. The crystal structure was solved from single crystal X-ray data and refined on F^2, $R_1 = 3.08$. The structure consists of layers made up by three building blocks, $[CoO_4Br_2]$, $[SbO_3Br]$, and $[SbO_3]$ that are connected via edge- and corner-sharing so that structural Co–Co dimers are formed. The layers have no net charge and are only weakly connected by van der Waals forces to adjacent layers. Above ~25 K the magnetic susceptibility is independent of the magnetic field and can be very well described by a Curie–Weiss law. Below 25 K the susceptibility passes through a maximum and decreases again that is typical for the onset of long-range antiferromagnetic correlations. Long-range antiferromagnetic ordering is observed below $T_N \sim 9$ K indicating substantial inter-dimer exchange coupling between Co–Co dimers within the layers. However, according to the heat capacity results only a minute fraction of the entropy is associated with the long-range ordering transition. The phonon anomalies observed for $T < 6$ K in Raman scattering and an anomaly in the specific heat point to a structural instability leading to a loss of inversion symmetry at lowest temperatures.

1. Introduction

A synthesis concept developed for searching new low-dimensional magnetically frustrated inorganic compounds has successfully been applied during the past years [1–7]. The concept is based on forming oxo-chlorides/oxo-bromides comprising *p*-element cations that carry a stereochemically active lone-pair of electrons (e.g. Te^{4+}, Se^{4+}, Sb^{3+}). The nature and the steric requirements of the lone-pair will cause one-sided coordination around the lone-pair cation [8]. The *p*-element lone-pair cations are most often bonded only to oxygen atoms in oxo-bromides/oxo-chlorides due to their high Lewis acid strength. Late transition metal cations introduced to lone-pair element oxo-halide systems display more affinity for halides [1–7]. It is found to be common in

our previous studies on oxo-halides that chlorine/bromine ions form only a single bond and act as terminating species that reside together with the lone-pairs in large non-bonding regions in the structure [9,10]. Hence, the combination of lone-pairs and halide ions is an efficient tool in order to open up the crystal structures and to increase the possibility for finding new low-dimensional arrangements. In this way also the magnetic dimensionality is influenced that may create unusual magnetic behavior.

The search for novel low-dimensional compounds in the $Co^{2+}–Sb^{3+}–O–X$ (X = halide ion) system resulted in the new compound $CoSb_2O_3Br_2$. To the best of our knowledge it is the first described Co^{2+} containing antimony oxo-halide. $CoSb_2O_3Br_2$ comprises structural $Co^{2+}–Co^{2+}$ dimers reminding of the $Cu^{2+}–Cu^{2+}$ dimers in $CuTe_2O_5$ that are also isolated by surrounding lone-pair cations [11,12].

2. Experimental

Single crystals and powder of $CoSb_2O_3Br_2$ were obtained in sealed evacuated silica tubes from Sb_2O_3 (Sigma-Aldrich, 99%) and

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CoBr$_2$ (Research chemicals Ltd, 98%). Mixtures of Sb$_2$O$_3$ and CoBr$_2$ in a molar ratio of 1:1 were heat treated in a muffle furnace at 400 °C for 192 h, the amount of starting materials was 0.3 g. The synthesis product contained dark blue CoSb$_2$O$_3$Br$_2$ single crystals and dark blue crystalline powder of the same phase. The fraction of single crystals was about 10% and the rest powder. Attempts were made to synthesize CoSb$_2$O$_3$Cl$_2$ and CoSb$_2$O$_3$I$_2$ with similar methods, however those attempts where not successful.

The chemical composition of the new oxo-halide was characterized in a scanning electron microscope (SEM, JEOL 820) equipped with an energy-dispersive spectrometer (EDS, LINK AN10000).

Single crystal X-ray diffraction data were collected on an Oxford Xcalibur3 system, mounted with a Mo$K\alpha$ source. Integration of the reflection intensities and absorption correction were made using the software provided by the diffractometer manufacturer [13]. The structure was solved by direct methods (SHELXS97) [14] and refined by full matrix least squares on F^2 using the program SHELXL97 [15]. All illustrations were made with the program DIAMOND [16]. Crystallographic data for CoSb$_2$O$_3$Br$_2$ are shown in Table 1.

The samples used for susceptibility and heat capacity measurements where characterized by powder X-ray diffraction using a Guiner-Hägg focusing camera with subtraction geometry (Cu$K\alpha_1$ $\lambda = 1.54060$ Å). Silicon, $a = 5.430088(4)$ Å, was added as an internal standard. The recorded films were read in an automatic scanner and the data were evaluated using the program SCANPI [17] and PIRUM [18].

The magnetic susceptibilities of a polycrystalline sample ($m\sim 40$ mg) were measured in a MPMS SQUID magnetometer (Quantum Design) at various external fields in the temperature range $1.8 \text{ K} \leqslant T \leqslant 300 \text{ K}$. The heat capacities were determined in a PPMS system (Quantum Design) in the temperature range $1.8 \text{ K} \leqslant T \leqslant 50 \text{ K}$ in magnetic fields up to 6 T on a randomly oriented polycrystalline sample of ~ 2 mg. The addenda heat capacities of a minute amount of Apiezon N grease used to thermally couple the sample to the platform and the heat capacity of the platform were determined in a separate run and subtracted.

Raman scattering experiments were performed in quasi-backscattering geometry with a laser power of $P = 0.5$ mW at $\lambda = 532$ nm excitation wavelength and a focus diameter of $d = 100 \, \mu$m. Small single crystal samples of CoSb$_2$O$_3$Br$_2$ were attached to a cold finger of an evacuated cryostat allowing a temperature variation between 3.1 and 300 K. No evidence for changes in the Raman spectra was found for temperatures above 10 K. Therefore, we focussed our attention on the Raman spectra collected below 10 K. There was no evidence of polarization effects in the spectra. This is related to the symmetry of the excitations.

3. Results and discussion

3.1. Crystal structure

The new layered compound CoSb$_2$O$_3$Br$_2$ crystallizes in the triclinic system, space group $P-1$, and the layers extend in the ac-plane. EDS analyses based on 6 different crystals confirm the presence and stoichiometry of the heavy elements to be 41.6 ± 1.4 at% Sb, 21.6 ± 2.1 at% Co, 36.8 ± 2.7 at% Br. The silicon content is at the detection limit for the instrument indicating that there was no substantial reaction with the silica tubes. Those values are in reasonable agreement with the structural refinement that gives 40 at% Sb, 20 at% Co, and 40 at% Br. The bromide ions and the lone-pairs of electrons E belonging to Sb^{3+} cation, protrude from the layers into non-bonding regions of the structure, see Fig. 1. The shortest cation–anion distances between adjacent layers; Sb(1)$\cdots$Br(2) = 3.79(6) Å, Sb(2)$\cdots$Br(2) = 4.24(7) Å are markedly longer than the cation–cation separation within the layers; Sb(2)$\cdots$Sb(2) = 3.18(5) Å, Sb(1)$\cdots$Sb(1) = 3.26(3) Å, Co(1)$\cdots$Co(1) = 3.39(1) Å. The cation–cation separation within the layers are of about the same distances as the cation–anion interlayer distances indicating absence of significant bonding contact in between the adjacent layers and suggest that only weak van der Waals forces connect the layers to each other in the structure. Each layer may thus be considered as an infinite two-dimensional neutral molecule.

Bond valence sum (BVS) calculations were used as a guide to decide which ligands should be considered as belonging to the primary coordination sphere of Sb^{3+}. The bond valence contribution for each atom is listed in Table 2 and BVS for each of the ligands can be found in Table 3.
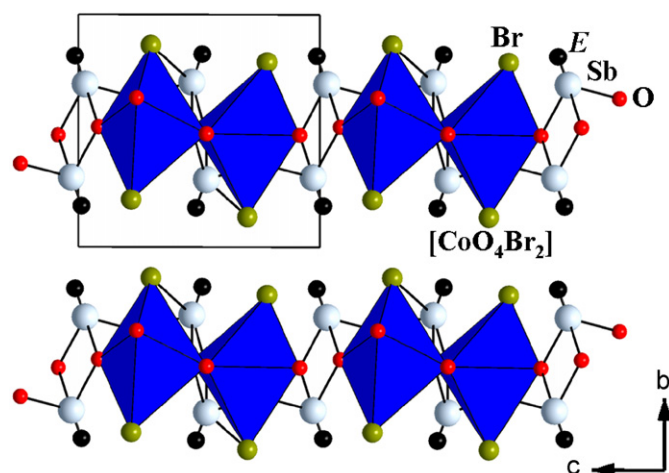
Table 1
Crystal data for CoSb$_2$O$_3$Br$_2$

Formula weight	510.25
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal system	Triclinic
Space group	$P-1$
Unit cell dimensions (Å, deg)	$a = 5.306(3)$, $\alpha = 88.54(3)$
	$b = 7.812(4)$, $\beta = 82.17(3)$
	$c = 8.0626(10)$, $\gamma = 80.32(4)$
Volume (Å^3)	326.3(3)
Z	2
Density (calc) (g/cm^3)	5.193
Adsorption coefficient (mm^{-1})	22.89
Absorption correction	Multi-scan
$F(000)$	446
Crystal color	Dark blue
Crystal habit	Plate like
Crystal size	$0.04 \times 0.04 \times 0.02$
θ range for data collection (deg)	4.36–27.10
Index range	$-6 \leqslant h \leqslant 6$, $-9 \leqslant k \leqslant 10$ $-10 \leqslant l \leqslant 10$
Reflections collected	7126
Independent reflections	1421 [$R(\text{int}) = 0.0702$]
Completeness to θ	0.991
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	1421/0/73
Goodness-of-fit on F^2	0.964
Final R indices [$I > 3\sigma(I)$]	$R = 0.0308$
	w$R = 0.0652$
R indices (all data)	$R = 0.0437$
	w$R = 0.0659$
Largest difference peak and hole	1.204 and -1.256 (e Å^{-3})

Fig. 1. Structure of CoSb$_2$O$_3$Br$_2$ viewed along the a-axis. The layers are separated by non-bonding volumes occupied by bromide ions and stereochemically active lone-pair electrons of Sb^{3+}.