



Structure and magnetism of novel mixed-anionic-group compounds $M_2(\text{SeO}_3)(\text{Te}_3\text{O}_7)$ ($M = \text{Co}^{2+}, \text{Ni}^{2+}$)



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ARTICLE INFO

Article history:

Received 12 July 2017

Received in revised form

29 August 2017

Accepted 1 September 2017

Available online 4 September 2017

Keywords:

A. Selenite-tellurites

B. Hydrothermal method

C. Crystal structure

C. Magnetic properties

ABSTRACT

Novel mixed-anionic-group compounds $M_2(\text{SeO}_3)(\text{Te}_3\text{O}_7)$ ($M = \text{Co}^{2+}, \text{Ni}^{2+}$) are successfully synthesized by a conventional hydrothermal method. Two compounds are isostructural which crystallize in the orthorhombic system of a space group $Pnma$. The framework shows a $(\text{MO}_6)_\infty$ chain structure along the b -axis, while SeO_3 groups are isolated and Te_3O_7 groups form the $(\text{Te}_3\text{O}_7)_\infty$ chains running along the a -axis. This is the first time to realize transition-metal compounds coexisting with Se^{4+} and Te^{4+} anionic groups. Magnetic measurements show that $\text{Co}_2(\text{SeO}_3)(\text{Te}_3\text{O}_7)$ possesses an antiferromagnetic ordering at ~ 11 K, while $\text{Ni}_2(\text{SeO}_3)(\text{Te}_3\text{O}_7)$ exhibits a similar antiferromagnetic ordering at ~ 31 K. Also, the fitting of magnetic susceptibility using a spin-chain model gives the exchange coupling $J/k_B = -1.515$ K for $\text{Co}_2(\text{SeO}_3)(\text{Te}_3\text{O}_7)$ and $J/k_B = -8.963$ K for $\text{Ni}_2(\text{SeO}_3)(\text{Te}_3\text{O}_7)$, respectively.

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1. Introduction

Transition metal selenites and tellurites have attracted much attention due to their rich structure chemistry and interesting magnetic properties. Usually selenium and tellurium in oxides have two postulated oxidation states of +4 and +6, in which the stereoactive lone-pair electrons of Se^{4+} and Te^{4+} can serve as “chemical scissors”, leading to the diversity of structural frameworks [1]. It is well-known that Se^{4+} anionic groups of selenites exist in two formations of $(\text{SeO}_3)^{2-}$ and $(\text{Se}_2\text{O}_5)^{2-}$, while Te^{4+} of tellurites often form $(\text{TeO}_3)^{2-}$, $(\text{TeO}_4)^{4-}$, and $(\text{TeO}_5)^{6-}$ anionic groups, which can also connect to each other, forming one-dimensional (1D) chains, two-dimensional (2D) sheets as well as three-dimensional (3D) reticular structures [2]. Although many selenites have been studied intensively, there are a few hydroxyl-free or halide-free transition-metal selenites including MSeO_3 ($M = \text{Cu}^{2+}, \text{Ni}^{2+}, \text{Co}^{2+}, \text{Mn}^{2+}$) [3,4], MSe_2O_5 ($M = \text{Cu}^{2+}, \text{Co}^{2+}, \text{Mn}^{2+}$) [5–7], Cu_2SeO_4 [8], $\text{ACu}(\text{SeO}_3)_2$ ($A = \text{Cd}^{2+}, \text{Hg}^{2+}$) [9], $\text{Na}_2\text{M}_2(\text{SeO}_3)_3$ ($M = \text{Ni}^{2+}, \text{Co}^{2+}$) [10], and $\text{Sr}_2\text{M}(\text{SeO}_3)_3$ ($M = \text{Cu}^{2+}, \text{Co}^{2+}$) [11,12]. Among these selenite compounds, Cu_2SeO_4 shows an unusual ferrimagnetic behavior, in

which magnetoelectric effects [8] and skyrmions can be observed due to a spin-chiral structure [13]. Similar to selenites, there are also a few hydroxyl-free or halide-free transition-metal tellurites including MTeO_3 ($M = \text{Cu}^{2+}, \text{Ni}^{2+}, \text{Co}^{2+}, \text{Mn}^{2+}$) [14,15], MTe_2O_5 ($M = \text{Cu}^{2+}, \text{Co}^{2+}, \text{Mn}^{2+}$) [16–18], $\text{M}_2\text{Te}_3\text{O}_8$ ($M = \text{Cu}^{2+}, \text{Ni}^{2+}, \text{Co}^{2+}, \text{Mn}^{2+}$) [19], $\text{Hg}_2\text{Cu}_3(\text{Te}_3\text{O}_8)_2$ [9], ACuTe_2O_6 ($A = \text{Sr}^{2+}, \text{Pb}^{2+}$) [20,21], and $\text{NaFe}(\text{TeO}_3)_2$ [22]. Among these tellurites, CuTe_2O_5 exhibits a spin-dimer structure, which shows a nonmagnetic spin-singlet ground state [23], while $\text{Co}_2\text{Te}_3\text{O}_8$ and $\text{Ni}_2\text{Te}_3\text{O}_8$ exhibit a typical honeycomb structure, showing an antiferromagnetic ordering at low temperature [19].

To explore new transition metal based oxides and to further investigate interesting magnetic phenomena, our current motivation is focused on selenite-tellurite compounds through a partial substitution of $(\text{SeO}_3)^{2-}$ or $(\text{TeO}_3)^{2-}$ for selenites or tellurites, respectively. Recently we have successfully synthesized two new selenite-tellurite compounds $M_2(\text{SeO}_3)(\text{Te}_3\text{O}_7)$ ($M = \text{Co}^{2+}$ and Ni^{2+}). It must be noted that no any transition-metal based compounds have been reported to exhibit a mixture of Se^{4+} and Te^{4+} anionic groups in their structural frameworks so far. To the best of our knowledge, $M_2(\text{SeO}_3)(\text{Te}_3\text{O}_7)$ ($M = \text{Co}^{2+}$ and Ni^{2+}) are the first transition-metal compounds coexisting with Se^{4+} and Te^{4+} anionic groups. Here we report their syntheses, structures and magnetic properties in detail.

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2. Experimental sections

2.1. Preparation of samples

Single crystals of $M_2(\text{SeO}_3)(\text{Te}_3\text{O}_7)$ ($M = \text{Co}^{2+}, \text{Ni}^{2+}$) were synthesized by a conventional hydrothermal method. A mixture of 0.5 mmol of $\text{CoCO}_3 \cdot x\text{H}_2\text{O}$ (2 N, 0.0595 g) or 0.5 mmol of $\text{Ni}(\text{OH})_2$ (2 N, 0.0464 g), 0.5 mmol of TeO_2 (3 N, 0.0798 g), 0.5 mmol of SeO_2 (3 N, 0.0555 g), and 5 mL of deionized water was sealed in autoclaves equipped with a Teflon liner (28 mL), respectively. The autoclaves were gradually heated to 210 °C, held for 4 days, and then cooled to room temperature at a rate of 4 °C/h for 2 days. The fuchsia block-shaped crystals of $\text{Co}_2(\text{SeO}_3)(\text{Te}_3\text{O}_7)$ with the size of 0.4 mm × 0.3 mm × 0.3 mm and yellow-orange block-shaped crystals of $\text{Ni}_2(\text{SeO}_3)(\text{Te}_3\text{O}_7)$ with the size of 0.3 mm × 0.2 mm × 0.2 mm were obtained separately and further dried at 60 °C for 2 h. The powdered samples were prepared by crushing small single crystals of $\text{Co}_2(\text{SeO}_3)(\text{Te}_3\text{O}_7)$ and $\text{Ni}_2(\text{SeO}_3)(\text{Te}_3\text{O}_7)$ separately, which were used for various physical measurements. The purity of powdered samples was confirmed by powder X-ray diffraction analysis (Fig. S1 in the Supporting Information).

2.2. X-ray crystallographic studies

Small crystals of $M_2(\text{SeO}_3)(\text{Te}_3\text{O}_7)$ ($M = \text{Co}^{2+}, \text{Ni}^{2+}$) with a size of 0.2 mm × 0.05 mm × 0.05 mm were selected and mounted on glassy fibers for single crystal X-ray diffraction (XRD) measurements. Data collections were performed on Rigaku Mercury CCD diffractometer equipped with a graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 293 K. The data sets were corrected for Lorentz and polarization factors as well as for absorption by Multiscan method [24]. The crystal structure was solved using direct methods and refined by full matrix least-squares fitting on F^2 by SHELX-14 software [25]. The final refined structure parameters were checked by the PLATON program [26]. Crystallographic data, structural refinements and important bond distances are summarized in Tables 1 and 2, respectively. More crystallographic data on the compounds are seen in the Supporting Information (Table S1 – S3).

2.3. Magnetic measurements

Powdered samples of $M_2(\text{SeO}_3)(\text{Te}_3\text{O}_7)$ ($M = \text{Co}^{2+}, \text{Ni}^{2+}$) were placed separately in a gel capsule sample holder suspending in a plastic drinking straw. Magnetic susceptibilities were measured

Table 1
Crystal data and structure refinement for $M_2(\text{SeO}_3)(\text{Te}_3\text{O}_7)$ ($M = \text{Co}^{2+}$ and Ni^{2+}).

Formula	$\text{Co}_2(\text{SeO}_3)(\text{Te}_3\text{O}_7)$	$\text{Ni}_2(\text{SeO}_3)(\text{Te}_3\text{O}_7)$
Fw	369.81	369.59
T, K	Room temperature	Room temperature
λ , Å	0.71073	0.71073
Space group	<i>Pnma</i>	<i>Pnma</i>
<i>a</i> , Å	9.037(7)	8.921(6)
<i>b</i> , Å	12.193(9)	12.073(9)
<i>c</i> , Å	8.184(6)	8.233(6)
α , deg	90	90
β , deg	90	90
γ , deg	90	90
<i>V</i> , Å ³	901.81(1)	886.71(1)
<i>Z</i>	8	8
D_{calcd} , g·cm ⁻³	5.448	5.537
μ , mm ⁻¹	17.270	18.070
GOF on F^2	1.139	1.175
R1, $wR2$ [$I > 2\sigma(I)$] ^a	0.0401, 0.1178	0.0398, 0.0977
R1, $wR2$ (all data)	0.0433, 0.1199	0.0403, 0.0979

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, and $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

Table 2
Selected bond lengths [Å] for $M_2(\text{SeO}_3)(\text{Te}_3\text{O}_7)$ ($M = \text{Co}^{2+}$ and Ni^{2+}).

Te(1)–O(1)	1.878(11)	Se(1)–O(2)#5	1.706(8)
Te(1)–O(6)	1.984(8)	Se(1)–O(5)	1.735(12)
Te(1)–O(6)#1	1.984(8)	Co(1)–O(1)#6	2.038(7)
Te(1)–O(3)#2	2.254(8)	Co(1)–O(2)#4	2.049(8)
Te(1)–O(3)#3	2.254(8)	Co(1)–O(4)	2.061(8)
Te(2)–O(4)	1.844(8)	Co(1)–O(3)#7	2.143(8)
Te(2)–O(3)	1.840(8)	Co(1)–O(4)#8	2.154(8)
Te(2)–O(6)#4	1.910(7)	Co(1)–O(5)#7	2.198(8)
Se(1)–O(2)	1.706(8)		
Te(1)–O(1)	1.895(10)	Se(1)–O(6)	1.722(9)
Te(1)–O(4)#1	2.014(7)	Se(1)–O(3)	1.752(11)
Te(1)–O(4)#2	2.014(7)	Ni(1)–O(1)	2.028(7)
Te(1)–O(5)#3	2.222(8)	Ni(1)–O(2)#4	2.055(8)
Te(1)–O(5)	2.222(8)	Ni(1)–O(6)#5	2.064(8)
Te(2)–O(5)	1.849(8)	Ni(1)–O(5)	2.076(8)
Te(2)–O(2)	1.851(8)	Ni(1)–O(2)#1	2.121(8)
Te(2)–O(4)	1.902(7)	Ni(1)–O(3)	2.162(8)
Se(1)–O(6)#3	1.722(9)		

Symmetry transformations used to generate equivalent atoms: $\text{Co}_2(\text{SeO}_3)(\text{Te}_3\text{O}_7)$: #1 $x, -y+3/2, z$; #2 $-x+1/2, y+1/2, z+1/2$; #3 $-x+1/2, -y+1, z+1/2$; #4 $-x, -y+1, -z$; #5 $x, -y+1/2, z$; #6 $x, y, z-1$; #7 $-x+1/2, -y+1, z-1/2$; #8 $-x, -y+1, -z-1$; #9 $x, -y+3/2, z+1$; #10 $x, y, z+1$; #11 $-x+1/2, y-1/2, z+1/2$. $\text{Ni}_2(\text{SeO}_3)(\text{Te}_3\text{O}_7)$: #1 $x-1/2, y, -z+1/2$; #2 $x-1/2, -y+3/2, -z+1/2$; #3 $x, -y+3/2, z$; #4 $-x+3/2, -y+1, z+1/2$; #5 $x-1/2, y, -z+3/2$; #6 $-x+3/2, -y+1, z-1/2$; #7 $x+1/2, y, -z+1/2$; #8 $x+1/2, y, -z+3/2$.

under an applied field of 1000 Oe from 300 to 2 K (temperature scan of 5 K/min) using a commercial Magnetic Property Measurement System (MPMS). Magnetization was measured at 2 K in applied field from 0 to 8 T (field scan of 0.1 T/step) using Quantum Design Physical Property Measurement System (PPMS).

3. Results and discussion

3.1. Structural analysis

Single crystal X-ray analysis reveals that $M_2(\text{SeO}_3)(\text{Te}_3\text{O}_7)$ ($M = \text{Co}^{2+}, \text{Ni}^{2+}$) crystallizes in the orthorhombic system of a space group *Pnma*. The unit cell parameters with $a = 9.037(7)$ Å, $b = 12.194(9)$ Å, $c = 8.184(6)$ Å for $\text{Co}_2(\text{SeO}_3)(\text{Te}_3\text{O}_7)$ and $a = 8.921(6)$ Å, $b = 12.073(9)$ Å, $c = 8.233(6)$ Å for $\text{Ni}_2(\text{SeO}_3)(\text{Te}_3\text{O}_7)$, respectively. Since they are isostructural, we selected compound $\text{Co}_2(\text{SeO}_3)(\text{Te}_3\text{O}_7)$ as a representative for the description of their structures. There are only one crystallographic Co, one Se, two Te sites in an asymmetrical unit (Fig. 1). The Co ion is coordinated by six oxygen atoms, forming a distorted CoO_6 octahedron with bond lengths ranging from 2.038(7) to 2.198(8) Å. Se atom is coordinated by three oxygen atoms, adopting a SeO_3 trigonal pyramid with bond lengths around 1.70 Å. Te1 atom is coordinated by five O atoms in a distorted Te1O_5 pentagonal-pyramidal geometry with three short bonds of around 1.95 Å and two long bonds of around 2.25 Å, while Te2 atom is coordinated by three O atoms in a distorted Te2O_3 trigonal pyramidal geometry with bond lengths around 1.85 Å. The bond valence sum (BVS) calculations give the rational value of 1.980 for Co, 4.215 for Te(1), 4.079 for Te(2), and 3.884 for Se, which are entirely close to their postulated oxidation states of +2, +4, +4, and +4.

As shown in Fig. 2, the 3D framework of $\text{Co}_2(\text{SeO}_3)(\text{Te}_3\text{O}_7)$ is constructed by CoO_6 octahedra, SeO_3 trigonal pyramids, Te1O_5 pentagonal-pyramids, and Te2O_3 trigonal pyramids, showing a chain structure along the *b*-axis, in which the Co-chains are separated by isolated SeO_3 and Te_3O_7 anionic networks and the shortest distance of Co··Co between neighboring chains is 5.849(1) Å, which is slightly shorter than that [5.8721(4) Å] of the interchain Ni··Ni of $\text{Ni}_2(\text{SeO}_3)(\text{Te}_3\text{O}_7)$. To check the linkages of polyhedra in the framework (Fig. 3a), it is noted that the Co-chains are not

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