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Synthesis and Crystal Structure of the Solid Solution $Co_3(SeO_3)_{3-x}(PO_3OH)_x(H_2O)$ Involving Crystallographic Split Positions of Se^{4+} and P^{5+}

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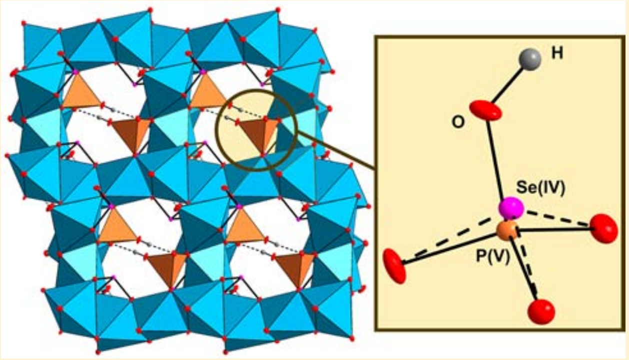
Supporting Information

ABSTRACT: Three new cobalt selenite hydroxo-phosphates laying in the solid solution $Co_3(SeO_3)_{3-x}(PO_3OH)_x(H_2O)$, with $x = 0.8$, $x = 1.0$, and $x = 1.2$ are reported. Single crystals were obtained by hydrothermal synthesis and the crystal structure was determined by single crystal X-ray diffraction. The structure can be described as a 3D framework having selenite and hydroxo-phosphate groups protruding into channels in the crystal structure. Se^{4+} and P^{5+} share a split position in the structure so that either SeO_3 groups having a stereochemically active lone pair or tetrahedrally coordinated PO_3OH groups are present. The OH-group is thus only present when the split position is occupied by P^{5+}. The crystal water is coordinated to a cobalt atom and TG and IR measurements show that the water and hydroxyl groups leave the structure at unusually high temperatures (>450 °C). Magnetic susceptibility measurements show antiferromagnetic coupling below 16 K and a magnetic moment of 4.02(3) μ_B per Co atom was observed.



1. INTRODUCTION

Transition metal phosphates have a rich and interesting structural chemistry. In most cases it is a combination of phosphate tetrahedra and transition metal octahedra, which build up the structural framework, and many different types of structures have been found: clusters as in $[Co(C_2H_4(NH_2)_2)_3][C_4H_{12}N_2]_{0.5}[(Mo_5O_{15})(HOPO_3)_2]\cdot 3H_2O$,[1] layers as in metal phosphates[2] and metal phosphonates,[3] or microporous frameworks as in $Zn_2Co_4(PO_4)_4(H_2O)_5\cdot 2H_2O$[4] and in molybdenum phosphates.[5] Phosphates also catch great interest for their applications as ion-exchangers and heterogeneous catalysts.[6−8] Furthermore, several phosphates containing transition metals have been proven to show interesting magnetic properties.[9−12] Selenium (IV) is an interesting p-element because of the stereochemically active lone pair caused by the Second order Jahn−Teller distortion (SOJT).[13,14] Most often Se^{4+} adopts a one-sided trigonal pyramidal coordination and the lone-pair occupy nonbonding space in the crystal structure.[15−17]

In this work we report on the synthesis, crystal structure, thermal stability, and magnetic properties of the solid solution $Co_3(SeO_3)_{3-x}(PO_3OH)_x(H_2O)$, $0.8 \leq x \leq 1.2$. To the best of our knowledge this is the first transition metal phosphate containing Se^{4+} and also the first case where Se^{4+} and P^{5+} occupy the same split position despite the fact that they have different coordination geometries.

There are several metal-oxo-phosphate compounds reported in the literature, where the phosphate group is partially replaced by an arsenate AsO_4 building unit, i.e., P^{5+} is replaced by As^{5+}. AsO_4 forms the same tetrahedral coordination polyhedra, but the As−O bond lengths are slightly longer, which may lead to changes in both crystal structure and physical properties. Example structures with mixed P/As positions are $(NH_4)[Fe(AsO_4)_{1-x}(PO_4)_xF]$,[18] $LiTiOAs_{1-x}P_xO_4$[19] and the mineral olivenite Cu_2AsO_4OH,[20] where some of the arsenate can be replaced by phosphate. In $K_2(HSeO_4)_{1.5}(H_2PO_4)_{0.5}$[21] another kind of solid solution has been reported, where Se^{6+} and P^{5+} occupy a mixed position. Both ions adopt the same tetrahedral coordination polyhedra with similar bond distances.

2. EXPERIMENTAL SECTION

Single crystals of (**1**) $Co_3(SeO_3)_{2.21}(PO_3OH)_{0.79}(H_2O)$, (**2**) $Co_3(SeO_3)_{1.84}(PO_3OH)_{1.16}(H_2O)$, and (**3**) $Co_3(SeO_3)_{2.02}(PO_3OH)_{0.98}(H_2O)$ were obtained by hydrothermal synthesis from anhydrous $CoCl_2$ (Sigma-Aldrich), SeO_2 (Alfa Aesar), and $(NH_4)H_2PO_4$ (STREM chemicals). The molar ratio of 6:4:1 was used for (**1**), 6:4:6 for (**2**), and 3:2:1 for (**3**), starting from 0.52g (4 mmol) $CoCl_2$. The powder was dissolved in 10 mL deionized water and subsequently put in a 23 mL Teflon lined autoclave. The reaction took place at 180 °C under autogenic pressure during 48 h. The autoclave was furnace cooled to room temperature and deep purple crystals of the title compound were filtered off, washed with water, and dried in air for further analysis. Attempts to synthesize the end components of the solid solution $Co_3(SeO_3)_{3-x}(PO_3OH)_x(H_2O)$ ($x = 3$ and $x = 0$) were unsuccessful; with low amounts of ammonium dihydrogen phosphate no precipitation was observed, and with a large

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excess of ammonium dihydrogen phosphate an unidentified pink powder was formed.

Single crystal X-ray diffraction experiments were carried out on an Oxford Diffraction Xcalibur3 diffractometer equipped with a graphite monochromator. The data collection was at 293 K using Mo Kα radiation, $\lambda = 0.71073$ Å. Absorption correction and data reduction were done with the software CrysAlis RED that also was employed for the analytical absorption correction.[22] The structure solution was carried out with SHELXS-97 and the refinement with SHELXL-97 in the WINGX environment.[23,24] Two crystals were investigated for each of **1** and **2**: **1a**, **1b**, **2a**, and **2b**. All atomic positions were refined anisotropically, except for atoms P1, Se3, and O5 in **1a**, **1b**, and **3**; and P2, Se2, and O12 in **2a**, **2b**, and **3**. As these Se and P atoms are very close to each other in the split position, the thermal parameters could not be refined because of overlapping electron density. As a consequence of the split position, the atoms O5 in **1** and O12 in **2** are only present when atoms P1 and P2, respectively, are present. The hydrogen atoms could not be located from the X-ray diffraction data and were added based on bond valence sum calculations[25,26] and geometrical considerations. Some restrictions were applied during refinement of the structural data; for compounds **1** and **3** the sum of the occupancies of the atoms Se3 and P1 was restricted to 1 and the occupancy for O5 and H5 was set equal to that of P1; for compounds **2** and **3** the sum of the occupancies of atoms P2 and Se2 was set to 1 and the occupancy of O12 was set equal to that of P2. Because of the low occupancy of P2 and the large electron density of Se2 beside it, the exact position could not be refined and was set to be in the center of the four surrounding oxygen atoms. Crystal data are reported in Table 1; atomic coordinates and isotropic temperature parameters for all atoms are given in the Supporting Information. The structural drawings are made with the program DIAMOND.[27]

IR spectra on **1** and **2** were recorded on a Varian 670-IR FTIR spectrometer for the range 390−4000 cm^{-1} at ambient temperature. The spectrometer was equipped with an attenuated total reflection (ATR) detection device with a single reflection ATR diamond element.

Thermogravimetric studies on **1** and **2** were performed in a Perkin-Elmer TGA7 unit in nitrogen using a heating rate of 10 °C/min. A Panalytical X'Pert PRO powder diffractometer was used for collecting powder diffraction data of the end products.

The magnetic susceptibility of a powder sample of (**1**) (~6.18 mg) was measured as function of temperature in the range 5−300 K in a magnetic field of 1000 Oe with a Physical Property Measurement System (PPMS, Quantum design). The measured susceptibilities were corrected for diamagnetic contributions (-104×10^{-6} emu/mol; Se^{4+}, -8×10^{-6} emu/mol; Co^{2+}, -13×10^{-6} emu/mol; P^{5+}, -1×10^{-6} emu/mol; O^{2-}, -4.6×10^{-6} emu/mol).[28]

Table 1. Crystal Data and Structure Refinement Parameters for (1a) $Co_3(SeO_3)_{2.21}(PO_3OH)_{0.79}(H_2O)$, (2a) $Co_3(SeO_3)_{1.84}(PO_3OH)_{1.16}(H_2O)$, and (3) $Co_3(SeO_3)_{2.02}(PO_3OH)_{0.98}(H_2O)$

compound formula[a]	**1a**	**2a**	**3**
Formula weight (g/mol)	548.24	536.56	542.32
Temperature (K)	293	293	293
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic
Space group	*P-1*	*P-1*	*P-1*
a (Å)	7.8971(3)	7.8766(3)	7.8843(4)
b (Å)	8.0377(3)	8.0351(3)	8.0391(4)
c (Å)	8.8398(4)	8.8494(3)	8.8404(4)
α (deg)	66.029(4)	66.147(4)	66.099(6)
β (deg)	68.616(4)	68.719(4)	68.666(6)
γ (deg)	69.286(3)	69.313(4)	69.339(6)
Volume (Å^3)	463.27(3)	463.08(3)	463.08(4)
Z	2	2	2
Density$_{calc.}$ (g cm^{-3})	3.930	3.862	3.889
Absorption coefficient (mm^{-1})	14.158	12.797	13.471
F(000)	509	500	504
Crystal color	Purple	Purple	Purple
Crystal habit	Block	Block	Block
Crystal size (mm^3)	0.08 × 0.07 × 0.04	0.05 × 0.04 × 0.03	0.19 × 0.18 × 0.04
Theta range for data collection (°)	4.33 − 32.04	3.20 − 33.43	3.20 − 32.25
Index ranges	$-9 \le h \le 11$	$-12 \le h \le 9$	$-11 \le h \le 10$
	$-11 \le k \le 11$	$-12 \le k \le 12$	$-11 \le k \le 11$
	$-13 \le l \le 12$	$-13 \le l \le 11$	$-12 \le l \le 13$
Reflections collected	4437	5112	4436
Independent reflections	2849	3240	2855
Data/restraints/parameters	2849/6/168	3240/6/166	2855/6/161
Goodness-of-fit on F^2	0.998	1.026	1.089
Final *R* indices[b]	$R_1 = 0.0301$	$R_1 = 0.0298$	$R_1 = 0.0251$
[I > 2sigma(I)]	$wR_2 = 0.0713$	$wR_2 = 0.0663$	$wR_2 = 0.0702$
R indices (all data)	$R_1 = 0.0389$	$R_1 = 0.0463$	$R_1 = 0.0309$
	$wR_2 = 0.0731$	$wR_2 = 0.0954$	$wR_2 = 0.0722$
Largest diff. peak and hole (eÅ^{-3})	1.164 and −0.995	1.328 and −1.372	0.945 and −0.976

[a] The final refinements of the crystal structures were performed with the formulas $Co_3Se_{2.21}P_{0.79}O_{10.72}$ for (**1**), $Co_3Se_{1.84}P_{1.16}O_{11.16}$ for (**2**), and $Co_3Se_{2.02}P_{0.98}O_{10.98}$ for (**3**). The hydrogen atoms could not be detected by X-ray diffraction and were inserted at geometrically optimized positions after the final refinement. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

3. RESULTS AND DISCUSSION

3.1. Structure Description. Compounds **1**, **2**, and **3** crystallize in the triclinic space group *P*-1. The crystal structure can be described as a three-dimensional framework having channels along [010] and [001]; the phosphate and selenium oxide building blocks protrude into those channels. The position of the H_2O and OH-groups are stabilized in the structure by formation of hydrogen bonds to surrounding oxygen atoms belonging to the framework.

The crystal structure description below is based on **1** if not otherwise stated. There are four crystallographically different cobalt atoms in the structure which all have distorted octahedral coordination. Co−O bond distances range 2.003(3)−2.295(3) Å, in good agreement with values observed in cobalt oxides such as CoO and $Co(PO_4)_2$.[29,30] The atom Co(2) coordinates one H_2O molecule resulting in the octahedral coordination polyhedron $Co[O_5(H_2O)]$. The Co(2)−O(7)H_2 bond distance is 2.091(3) Å that is similar to a normal Co−O bond which has also been reported in other cobalt hydrates.[10,31] The cobalt octahedra are connected by either corner or edge sharing and constitute the main framework of the compound. The phosphorus and selenium oxide building units are attached to this framework and protrude into channels in the crystal structure; see Figure 1. Selenium oxide adopts a one-sided three coordination due to the stereochemically active lone pair, which occupies the other side. The Se−O bond distances are in the range of 1.592(8)−1.724(3) Å.

There are two phosphorus positions, and in compound **1**, it is P1 that split with Se3, while in compound **2**, it is P2 that split with Se2 (see Figure 2). Compound **3** that has an intermediate chemical composition shows both kind of splitting. For compound **1**, two crystals were refined **1a** and **1b**. In **1a** the P1 position has an occupancy of 0.79(1) and in **1b** it has

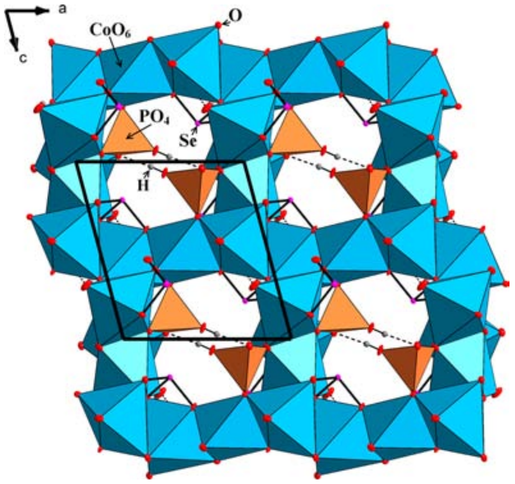

Figure 1. Overview of the crystal structure of **1** along [010]. For clarity the mixed Se/P positions are represented by PO_4 polyhedra only. The hydroxides located on the phosphate groups form hydrogen bonds to neighboring oxygen atoms within the channels.

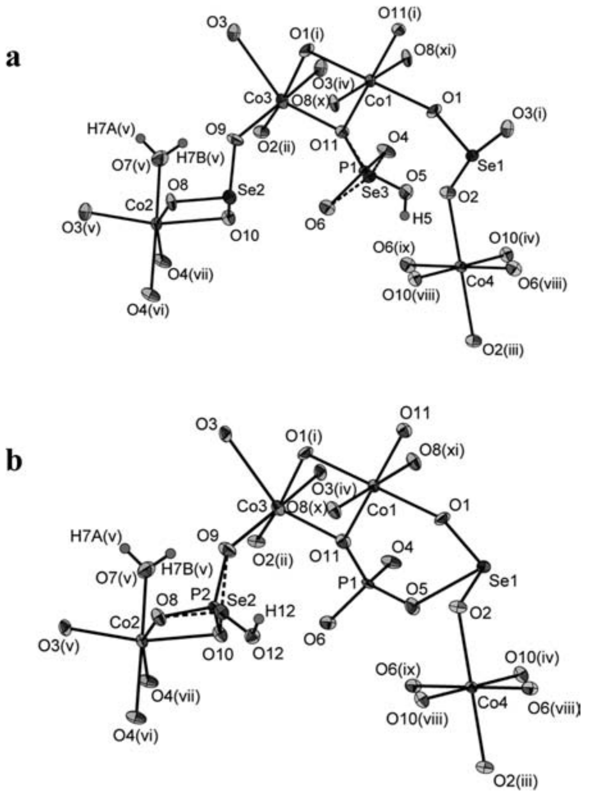

Figure 2. Asymmetric unit and selected symmetry equivalents for (a) compound **1** and (b) compound **2**. Hydrogen atoms are labeled in accordance with the number of the bonding oxygen atom. Symmetry codes: (i) 1−*x*,−*y*,1−*z* ; (ii) 1+*x*,*y*,*z*; (iii) −*x*,1−*y*,−*z*; (iv) 2−*x*,−*y*,1−*z*; (v) 2−*x*,1−*y*,1−*z*; (vi) *x*,1+*y*,*z*; (vii) 2−*x*,1−*y*,−*z*; (viii) −1+*x*,*y*,*z*; (ix) 1−*x*,1−*y*,−*z*; (x) 1−*x*,1−*y*,1−*z*; (xi) *x*,−1+*y*,*z*.

0.78(1). In compound **2**, the P2 position has an occupancy of 0.16(1) in **2a** and 0.17(1) in **2b**. Thus those crystals from the same batches show similar compositions. In compound **3**, the P1 position has an occupancy of 0.91(1) and the P2 position an occupancy of 0.07(1), so this composition ($x = 0.98$) that is in between **1** ($x = 0.79$) and **2** ($x = 1.16$) shows both types of split positions. Because of the different bonding distances toward neighboring oxygen atoms, the positions of phosphorus and selenium are not exactly the same and the selenium atom is slightly further away from the bonded oxygens (see Figure 3).

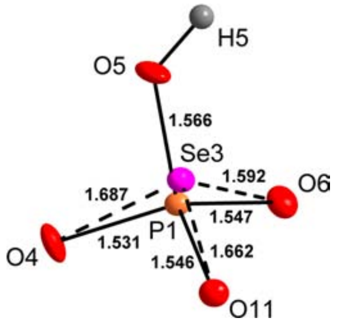

Figure 3. Detailed view of the split Se3/P1 position in **1a**. The occupancy is 79% P and 21% Se. The occupancies for O5 and H5 are the same as for P1. The Se atom is located slightly further away from the oxygens O4, O6, and O11 due to longer bonding distances for the SeO_3 building unit (dashed lines) compared to PO_4 (solid lines). Bond distances are given in Å.

In compounds **1** and **3**, O5 has the same occupancy as P1, as only phosphorus can adopt a tetrahedral coordination, whereas in the case of selenium, a trigonal pyramidal coordination is observed and the lone pair occupies the nonbonding space where O5 is located when P1 is present. Actually the position of the Se3 atom is not very accurate and the refined value gives unexpectedly short Se−O bonding distances and a high bond valence sum (BVS) parameter (4.7). This is due to the fact that the electron density of the phosphorus and selenium atom could not be clearly separated as they are very close to each other. Having mixed selenium oxide/phosphate positions is quite common for Se^{6+}, where the selenium and phosphorus atoms may take exactly the same position,[21] but to our knowledge, the present compounds are the first where P^{5+} replace Se^{4+}, which have very different coordination polyhedras. The $[PO_4]$ tetrahedra are fairly regular and P−O bond distances are in the range 1.531(5)−1.566(6) Å. There are two terminal oxygen atoms in the structure suitable for carrying hydrogen atoms; O5 and O7. In order to charge balance the chemical formula, O5 needs to be a hydroxide (OH^-) anion and O7 a water (H_2O) molecule. This is also supported by BVS calculations, which give low values for those oxygens (1.6 for O5 and 0.3 for O7). The low BVS value (1.6) for O6 can be explained by strong hydrogen bonding with the hydroxyl anion. The hydrogen atoms could not be located in the difference flourier map of the X-ray diffraction experiment due to the weak scattering of hydrogen atoms. The hydrogen positions were therefore inserted in geometrically optimized positions to allow hydrogen bonding with neighboring oxygen atoms; the O−H distance was kept fixed at around 0.8 Å.

Comparing the Se/P ratio obtained from EDS analysis with data from the structure refinements gives reasonably consistent results: 2.5(1) and 2.8(1), respectively, for compound **1** and 1.6(1) and 1.6(1), respectively, for compound **2**; see Supporting Information for EDS data.

3.2. IR and TG Measurements. The IR spectrum of **2** (not post heat treated) shows three strong maxima at 3510 cm^{-1}, 3245 cm^{-1}, and 3135 cm^{-1} corresponding to O−H stretching vibrations of the H_2O and OH^- groups. At 1617 cm^{-1} and 1206 cm^{-1} O−H bending vibrations of the H_2O and OH^-, respectively, can be observed. The strong peak at 1010 cm^{-1}

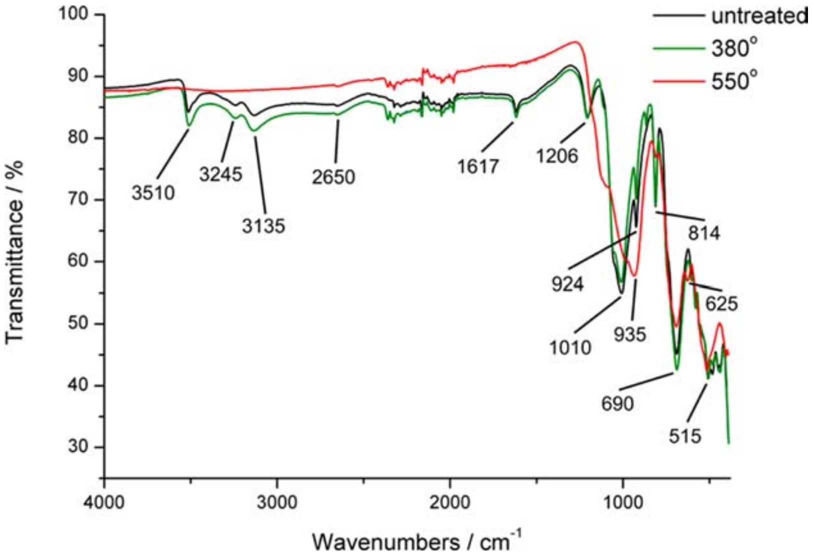

Figure 4. IR-measurements of compound **2** as-synthesized and heat-treated at 380 and 550 °C. The measurements show that the water molecules and hydroxo-groups are still present at 380 °C but have left at 550 °C.

originates from P—O stretching within the phosphate group. Peaks at lower wave numbers most likely belong to M—O (M = Se, Co) vibrations (see Figure 4). The sample was heated in air to 380 and 550 °C before further measurements. IR data shows that the H_2O and OH^- groups are present up to 380 °C. Heating from 380 to 550 °C makes the H_2O, OH, and SeO_2 groups leave, and an IR spectrum collected after heating to 550 °C shows that there are no OH or H_2O left (see Figure 4). The IR spectrum obtained for the as synthesized compound (**1**) (see Supporting Information) is very similar to the one for compound (**2**) showing that this compound also contains OH^- and H_2O groups.

Thermogravimetric analysis of compounds **1** and **2** shows that both materials are stable up to ca. 380 °C where they start to decompose (see Figure 5). The decomposition occurs in 3 main steps, and the first and third steps correspond most likely to loss of SeO_2. The second step starting around 450 °C involves a weight loss of ~6 wt % that is in good agreement with release of the crystal water and the hydroxide group; this temperature is unusually high for release of crystal water, but is consistent with the results from the IR measurements. The last decomposition step at 650—800 °C means that the remaining SeO_2 leaves the material. The total weight loss of compound **1** is a bit higher than for compound **2** and in good agreement with the results from the crystal structure determination and EDS analysis indicating that compound **1** contains more Se than compound **2**. Powder diffraction confirmed that the remaining products were CoO and $Co_3(PO_4)_2$.

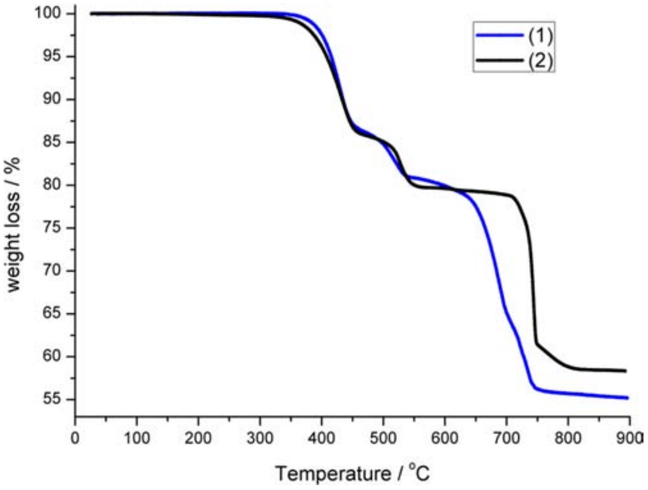

Figure 5. Thermogravimetric curve for the decomposition of compounds **1** and **2** in N_2(g). The compounds are stable up to ca. 380 °C. The decomposition takes place in three main steps; see text for discussion.

3.3. Magnetic Measurements.

The magnetic susceptibility of **1** corrected for diamagnetic contributions is shown in Figure 6. Field cooled and zero field cooled curves are identical in the measured temperature range 5—300 K. Paramagnetic behavior is observed in the range 22—300 K. A sharp antiferromagnetic transition appears at ca. 16 K and below 12 K the susceptibility increases again. The magnetic interactions between the cobalt ions are expected to be complex due to the intricate 3D cobalt oxide framework, and further studies such as neutron diffraction experiments would be needed to fully understand the magnetic structure.

Fitting the inverse susceptibility in the paramagnetic range from 22 to 300 K to the Curie—Weiss law $\chi_{\mathrm{mol}} = C/(T - \theta)$ gives $\theta = -76.83(1)$ K and $C = 6.06(1)$ emu·K·mol^{-1}. An effective magnetic moment of 4.02(3) μ_B per Co atom was calculated from $\mu_{\mathrm{eff}} = (C \cdot k_B/N_A)^{1/2} \cdot \mu_B$, where N_A is Avogadro's number and k_B Boltzmann's constant. The measured value of μ_{eff} is a bit low for a system containing Co^{2+} (high spin), but is too high for Co^{2+} (low spin). Similar anomalous values have, however, been observed also in other compounds containing Co^{2+}.[32]

4. CONCLUSION

Three compounds in the solid solution $Co_3(SeO_3)_{3-x}(PO_3OH)_x(H_2O)$, with (**1**) $x = 0.79(1)$, (**2**) $x = 1.16(1)$, and (**3**) $x = 0.98(1)$, have been successfully synthesized by hydrothermal techniques. The compounds crystallize in the triclinic space group *P*-1. The crystal structure can be described as a 3D framework built up from distorted cobalt octahedra, phosphate tetrahedra, and trigonal pyramidal

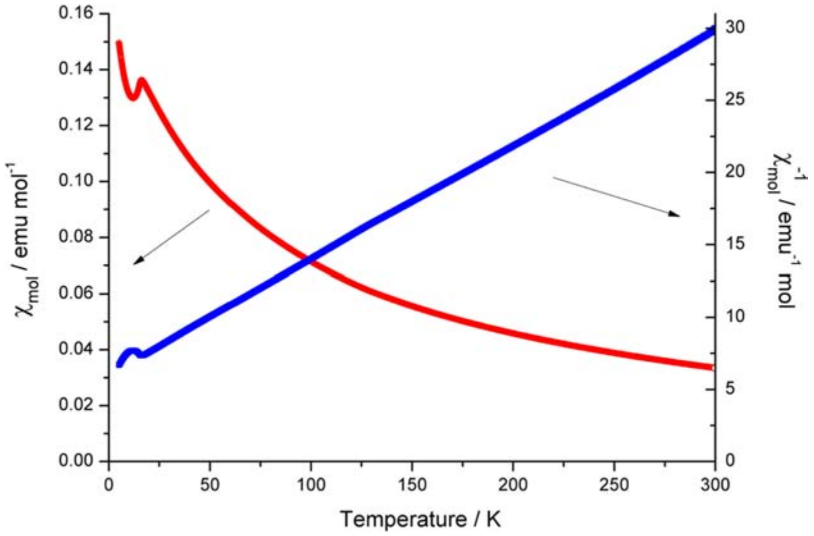

Figure 6. Magnetic susceptibility and inverse magnetic susceptibility of **1** measured at 0.1 T. Field cooled (FC) and zero field cooled (ZFC) curves are identical.

selenium oxide building blocks. The phosphate and selenium oxide building blocks are located inside small channels along the [010] and [001] directions. Se^{4+} and P^{5+} share a split position. For phosphorus there is a regular tetrahedral coordination in the $PO_3(OH)$ group and for selenium there is a one-sided trigonal bipyramidal coordination due to presence of the stereochemically active lone pair. The hydrogen atoms could not be identified by single crystal X-ray diffraction, but were added later based on geometrical considerations and with the help of bond valence sum calculations. A combination of TG and IR experiments shows that the crystal water and the hydroxide molecules leave the structure at temperatures higher than 450 °C, which must be considered unusually high. Magnetic measurements show an antiferromagnetic ordering below 16 K, and a magnetic moment of 4.02(3) μ_B per Co atom was observed.

One potential application of Se^{4+}/P^{5+} split positions could be to modify porous metal phosphates. The difference between a hydrogen phosphate group that can form hydrogen bonds and a selenium oxide building block with its stereochemically active lone pair that occupy a volume close to that of an oxygen atom is quite remarkable, and therefore partial replacement in such structures could lead to changes in, e.g., the catalytic properties or the ion exchange properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Atomic coordinates, selected bond lengths (Å), and angles (°); results from bond valence sum (BVS) calculations; EDS and IR measurements. Further details on the crystal structure investigation of **1**−**3** can be obtained from the Fachinformationszentrum Karlsruhe, Abt. PROKA, 76344 Eggenstein-Leopoldshafen, Germany (fax +49−7247−808−666; E-mail: crysdata@fiz-karlsruhe.de) on quoting the depository numbers CSD-426099 for **1a**, CSD-CSD-426598 for **1b**, CSD-426100 for **2a**, CSD-426599 for **2b**, CSD-426600 for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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