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A Low Temperature Method for the Synthesis of New Lead Selenite Chlorides: $Pb_3(SeO_3)(SeO_2OH)Cl_3$ and $Pb_3(SeO_3)_2Cl_2$

Yetta Porter and P. Shiv Halasyamani*

Department of Chemistry, University of Houston, 4800 Calhoun Boulevard, Houston, Texas 77204-5641

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Metal oxychlorides are of great interest due to their intercalation behavior, high-temperature superconductivity, optical properties, and interesting crystal chemistry.[1−10] For example, a variety of amines have been intercalated into FeOCl, TiOCl, VOCl, and LnOCl (Ln = Ho, Er, Tm, and Yb).[1−3] In addition, $(Ca,Na)_2CuO_2Cl_2$[11] and $(Ca,Na)_2CaCu_2O_4Cl_2$[12] have been shown to be high Tc materials, whereas $BiSeO_3Cl$ is SHG active.[6] Metal oxychlorides are synthesized either through solid-state techniques,[13,14] hydrothermally,[15] via chemical transport reactions,[16] or in the case of LnOCl by a two step pyrohydrolysis procedure.[2,17] Elevated temperatures (>250 °C), and in the case of solid-state reactions (>700 °C), are usually employed. We have developed a low-temperature (160 °C) aqueous method for the synthesis of new mixed-metal oxychlorides. In this communication, we report the syntheses, structures, and characterization of two new lead selenite chlorides, $Pb_3(SeO_3)(SeO_2OH)Cl_3$ and $Pb_3(SeO_3)_2Cl_2$. In addition, we demonstrate that an irreversible transformation occurs between the two materials.

Both $Pb_3(SeO_3)(SeO_2OH)Cl_3$ and $Pb_3(SeO_3)_2Cl_2$ were synthesized by using a low-temperature aqueous method. For $Pb_3(SeO_3)(SeO_2OH)Cl_3$, H_2SeO_3 (Aldrich, 98%) (0.4818 g, 3.74×10^{-3} mol) and $PbCl_2$ (Mallinckrodt, 99.8%) (0.5194 g, 1.87×10^{-3} mol) were combined in 5 mL of distilled water. For $Pb_3(SeO_3)_2Cl_2$, Na_2SeO_3 (Alfa, 99%) (0.2931 g, 1.69×10^{-3} mol) and $PbCl_2$ (0.7069 g, 2.54×10^{-3} mol) were dissolved in 5 mL of distilled water. The respective solutions were refluxed overnight at 160 °C and cooled to room temperature over a period of 2 h. For $Pb_3(SeO_3)(SeO_2OH)Cl_3$ and $Pb_3(SeO_3)_2Cl_2$, colorless parallelepiped-shaped crystals and colorless prismatic crystals[18] (the only products from the reactions) were recovered, by filtration, in 62% and 81% yields, respectively, based on Pb. The crystals were thoroughly washed with H_2O. The powder X-ray diffraction patterns on the products are in agreement with the generated pattern from the single-crystal data (see Supporting Information).

Both $Pb_3(SeO_3)(SeO_2OH)Cl_3$ and $Pb_3(SeO_3)_2Cl_2$ are pseudo-layered materials, consisting of sheets of lead−oxychloride polyhedra linked to selenium−oxide groups. In both materials, the Pb^{II} cations are bonded to oxygen and chloride ranging from 5- to 7-fold coordination, whereas the Se^{IV} are connected solely to oxygen. $Pb_3(SeO_3)(SeO_2OH)Cl_3$ consists of $[PbCl_{2/3}O_{4/4}O_{1/2}]^{1.667-}$, $[PbCl_{1/1}Cl_{2/2}O_{4/4}]^{2-}$, and $[PbCl_{1/3}O_{4/4}]^{0.333-}$ anions connected to $[SeO_{1/2}O_{2/4}]^{2+}$ and $[SeO_{2/4}OH]^{2+}$ cations. $Pb_3(SeO_3)_2Cl_2$ consists of $[PbCl_{2/2}O_{2/3}O_{4/4}]^{2.333-}$ and two $[PbCl_{1/2}O_{1/3}O_{4/4}]^{1.167-}$ anions linked to two $[SeO_{2/4}O_{1/3}]^{2.33+}$ cations. The Pb−O and Pb−Cl bond distances range from 2.44(2) to 2.758(11) Å and 2.822(6) to 3.089(2) Å, respectively, with long Pb−Cl interactions (>3.2 Å) occurring between the layers. The Se−O bond distances range from 1.652(8) to 1.80(2) Å. An important difference between the two materials is the occurrence of a $SeO_2(OH)$ group in $Pb_3(SeO_3)(SeO_2OH)Cl_3$. Both Pb^{II} and Se^{IV} are in asymmetric coordination environments attributable to their nonbonded electron pair (see Supporting Information). Infrared Data: $Pb_3(SeO_3)(SeO_2OH)Cl_3$ (ν_{Pb-O} (cm^{-1}) 712, 472, and 454; ν_{Se-O} (cm^{-1}) 823, 807, 638, and 597; ν_{Se-OH} (cm^{-1}) 1154), $Pb_3(SeO_3)_2Cl_2$ (ν_{Pb-O} (cm^{-1}) 706 and 463; ν_{Se-O} (cm^{-1}) 828 and 627). The stretches are consistent with those reported earlier.[22−24]

An interesting feature of the materials is the conversion of $Pb_3(SeO_3)(SeO_2OH)Cl_3$ to $Pb_3(SeO_3)_2Cl_2$ with the concomitant loss of HCl. This conversion is shown schematically in Figure 1a and b. We assume that the singly bonded chloride on the $[Pb\mathbf{Cl_{1/1}}Cl_{2/2}O_{4/4}]^{2-}$ group and the hydrogen on $[SeO_{2/4}\mathbf{OH}]^{2+}$ are

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* To whom correspondence should be addressed.

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(18) For $Pb_3(SeO_3)(SeO_2OH)Cl_3$ ($0.06 \times 0.14 \times 0.16$ mm) and $Pb_3(SeO_3)_2Cl_2$ ($0.06 \times 0.16 \times 0.16$ mm), colorless crystals were used. Single-crystal data were collected on Siemens SMART diffractometers equipped with a 1K CCD area detector using graphite monochromated Mo Kα radiation at 293 K. The data were integrated using the Siemens SAINT[19] program, with the intensities corrected for Lorentz, polarization, air absorption, and absorption attributable to the variation in path length through the detector faceplate. ψ-scan absorption corrections were applied. The structures were solved by direct methods using SHELXS-97[20] and refined using SHELXL-93.[21] Crystal data for $Pb_3(SeO_3)(SeO_2OH)Cl_3$: monoclinic, $P2_1/m$, $a = 7.7856(9)$ Å, $b = 5.6264(6)$ Å, $c = 12.4130(14)$ Å, $\beta = 99.057(2)°$, $V = 536.97(10)$ Å^3, $Z = 2$, $R(F) = 0.055$, GOF = 1.151. Crystal data for $Pb_3(SeO_3)_2Cl_2$: monoclinic, $C2/c$, $a = 13.4213(11)$ Å, $b = 5.5809(5)$ Å, $c = 13.0000(11)$ Å, $\beta = 94.301(14)°$, $V = 971.00(2)$ Å^3, $Z = 4$, $R(F) = 0.031$, GOF = 1.001.

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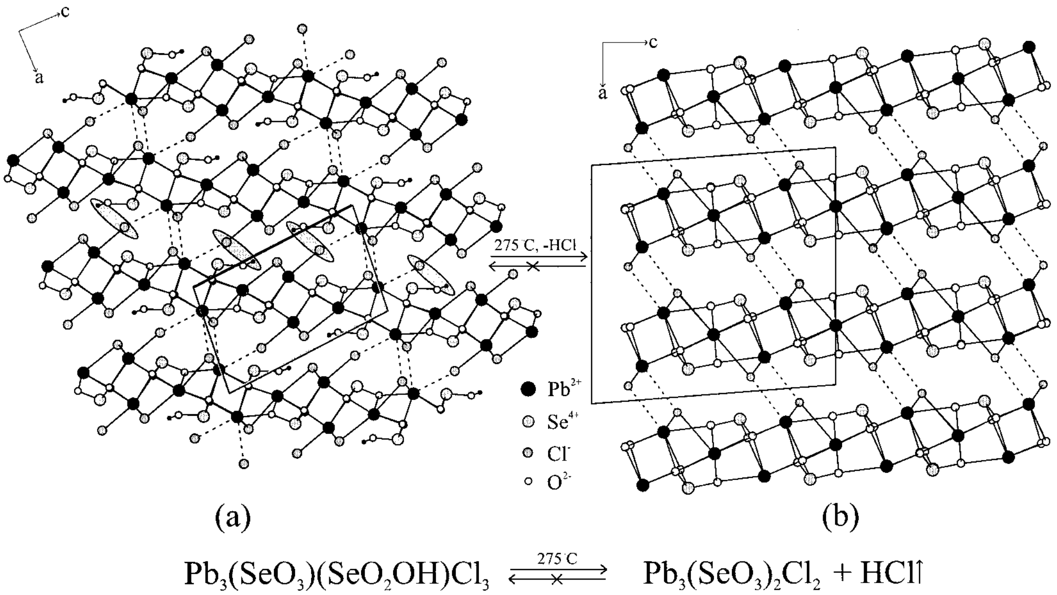

Figure 1. (a) Ball-and-stick representation of $Pb_3(SeO_3)(SeO_2OH)Cl_3$. The dashed lines indicate long Pb−Cl interactions (>3.2 Å). The shaded ellipse highlights the HCl atoms lost during the conversion of $Pb_3(SeO_3)(SeO_2OH)Cl_3$ to $Pb_3(SeO_3)_2Cl_2$. (b) Ball-and-stick representation of $Pb_3(SeO_3)_2Cl_2$. The dashed lines indicate long Pb−Cl interactions (>3.2 Å).

removed, producing the HCl. Thermogravimetric measurements on $Pb_3(SeO_3)(SeO_2OH)Cl_3$ revealed an initial weight loss of 3.83% at 230 °C; this weight loss is consistent with the removal of one molecule of HCl per formula unit−% calcd (% obsvd) 3.71 (3.83). Powder XRD measurements on the calcined material revealed a pattern consistent with $Pb_3(SeO_3)_2Cl_2$. The conversion is also consistent with the initial synthetic conditions for both materials. $Pb_3(SeO_3)(SeO_2OH)Cl_3$ was synthesized under acidic conditions (pH = 2) with $PbCl_2$ and H_2SeO_3 as reagents, whereas $Pb_3(SeO_3)_2Cl_2$ was synthesized under basic conditions (pH = 8) with $PbCl_2$ and Na_2SeO_3 as reagents. The conversion from $Pb_3(SeO_3)(SeO_2OH)Cl_3$ to $Pb_3(SeO_3)_2Cl_2$ is irreversible, as adding 0.5 M HCl to polycrystalline $Pb_3(SeO_3)_2Cl_2$ did not produce $Pb_3(SeO_3)(SeO_2OH)Cl_3$. Furthermore, $Pb_3(SeO_3)_2Cl_2$ did not react with more dilute HCl solutions.

In summary, we have demonstrated that a low-temperature aqueous method can be used to synthesize new lead selenite chlorides. In addition, we have demonstrated that a conversion between $Pb_3(SeO_3)(SeO_2OH)Cl_3$ and $Pb_3(SeO_3)_2Cl_2$ occurs at elevated temperatures. We are in the process of extending the technique to other post-transition metal halides.

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Supporting Information Available: Powder X-ray diffraction data (calculated and experimental), ORTEP diagrams, thermogravimetric data, and crystallographic information (in CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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