

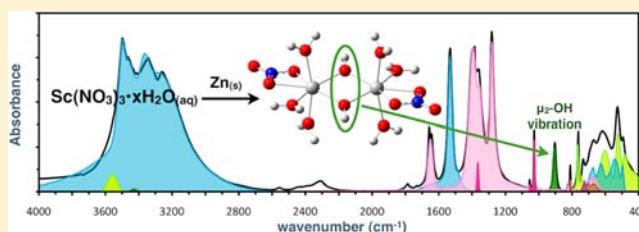
# [Sc<sub>2</sub>(μ-OH)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>: Aqueous Synthesis and Characterization

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## Supporting Information

**ABSTRACT:** [Sc<sub>2</sub>(μ-OH)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> has been synthesized from an aqueous scandium nitrate solution by using zinc powder as a reducing agent for nitric acid, which drives an increase in pH and forces the condensation of aqua scandium cations. This preparative route readily produces gram-scale samples with yields near 65%. A single-crystal X-ray diffraction study reveals a structure characterized by a hydroxo-bridged Sc dimer. The FTIR spectrum of the compound has been modeled via ab initio computations, allowing the identification of signature IR peaks. Some initial observations on the thermal transformation of the compound to Sc<sub>2</sub>O<sub>3</sub> are also reported.



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## INTRODUCTION

Cursory examination of the Pourbaix diagram of scandium, which summarizes its aqueous speciation, reveals a rather simple behavior. The oxidation state of the metal is fixed at +3. In highly acidic solutions, the simple monomeric aqua ion is the dominant species, and at modestly higher pH levels, i.e., ~4, the hydroxide Sc(OH)<sub>3</sub> begins to precipitate.<sup>1</sup> At intermediate pH values, just below that for Sc(OH)<sub>3</sub> precipitation, speciation appears to be more complex than that portrayed in the Pourbaix diagram, as evidence exists for formation of positively charged monomeric and polymeric hydroxo species.<sup>2</sup>

In this contribution, we describe a simple preparation of the salt [Sc<sub>2</sub>(μ-OH)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>, which has been isolated from an aqueous solution in the aforementioned intermediate pH region. Structural analysis reveals a dimeric scandium hydroxide motif, which forms without complex stabilizing ligands. During the past few decades, preparative, speciation, and structural studies of scandium oxo/hydroxo complexes have brought new understanding to the solution chemistry of scandium. For example, Ilyukhin and co-workers have synthesized the compounds [Sc(OH)(H<sub>2</sub>O)<sub>5</sub>]<sub>2</sub>X<sub>4</sub>·2H<sub>2</sub>O (X = Cl, Br) by simply dissolving scandium chloride or bromide in propanol or isopropanol.<sup>3</sup> The structures of these compounds are characterized by dimers comprising two seven-coordinate scandium centers and two bridging hydroxo ligands. The coordination environment of each scandium atom also includes five aqua ligands. The X halides do not directly coordinate to scandium, although they do participate in the three-dimensional hydrogen bonding framework of the structure. More recently, several structures of scandium nitrate, stabilized through incorporation of crown ethers, have been isolated from organic solvents.<sup>4</sup> Two examples are [Sc(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub>·15-crown-5 and [Sc(NO<sub>3</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>·12-crown-4. The structures of each of these

materials contain eight-coordinate scandium environments built from aqua and bis-ligated nitrate ligands. The crown ethers are associated with the coordination complexes through hydrogen bonding. These structures are consistent with the existence of monomeric scandium species in solution. In addition, the compound [Sc<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>(OH)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>·12-crown-4 has been isolated as a secondary product in low yield. Its structure contains a dimer unit of two seven-coordinate scandium atoms connected by two hydroxo bridges; each scandium is also coordinated by a bidentate nitrate ligand and three aqua ligands. As with the other crown-ether derivatives, 12-crown-4 associates with the coordination complex through hydrogen bonding. Unfortunately, the mixture of crown ether and organic solvents precludes a direct comparison to the hydrolysis and condensation chemistry of scandium species in aqueous solutions. Moreover, the efficacy of the syntheses of the crown-ether materials is consistently limited by a lack of reproducibility and very poor yields. The preparative method described here is the first example of an organic-free aqueous synthesis of the pure inorganic product [Sc<sub>2</sub>(μ-OH)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> at gram scale and in high yield.

The structural data enable a detailed computational assessment of the infrared absorption spectrum of the compound, providing a means to define signature spectral features arising from the dimer. Pathways for conversion of the dimer to Sc<sub>2</sub>O<sub>3</sub> via thermal treatment are also examined. In particular, hydrothermal treatment offers a means to effectively remove HNO<sub>3</sub> at relatively low temperatures, making simple dehydration the limiting step in conversion of the salt to the oxide. This report supports activities toward the development of scandium compounds as catalysts for aqueous-based

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synthetic organic reactions,<sup>5</sup> ongoing interest in scandium geochemistry,<sup>6</sup> and our own efforts covering the aqueous chemistry of oxo/hydroxo nanoclusters.<sup>7</sup> Extending this nanocluster chemistry to scandium could provide a unique pathway for the preparation of very high-quality scandium oxide films, which finds interest for use in optics and electronics manufacturing.<sup>8</sup>

## METHODS

**[Sc<sub>2</sub>(μ-OH)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> Synthesis.** Sc(NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O (Stanford Materials, 99.9%) was heated at 800 °C for 10 h to determine the hydration number *x*. A 20 mL, 1.0 M Sc<sup>3+</sup>(aq) initial solution was prepared by dissolving a proper amount of Sc(NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O in high-purity H<sub>2</sub>O (18.2 MΩ cm). A 0.4904 g sample of zinc metal powder (Alfa Aesar, 99.9%) was then added to the clear scandium solution. The reaction mixture was stirred overnight to ensure complete dissolution of the zinc powder. The resulting clear solution was then filtered into a crystallization dish and allowed to stand. As water evaporated and the solution became more concentrated, millimeter-sized colorless crystals formed. They were physically isolated for single-crystal X-ray diffraction studies.

A polycrystalline mixture containing [Sc<sub>2</sub>(μ-OH)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> and Zn(NO<sub>3</sub>)<sub>2</sub> was produced by complete evaporation of the water. Zn(NO<sub>3</sub>)<sub>2</sub> was then selectively removed by washing the mixture with isopropanol.

[Sc<sub>2</sub>(μ-OH)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> was also prepared by slowly adding 1.0 M NaOH(aq) to 1.0 M Sc(NO<sub>3</sub>)<sub>3</sub>(aq) to a final ratio of 1 OH<sup>-</sup>(aq): 1 Sc<sup>3+</sup>(aq). The mixture was allowed to stand. As the water evaporated, a precipitate formed. The resulting solid was then washed with isopropanol and dried in air for 5 h.

**X-ray Crystallography.** Single crystal X-ray diffraction data were collected at 173 K on a Bruker Apex CCD diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å). The space group was determined on the basis of intensity statistics. The structure was solved by direct methods and Fourier techniques and refined on F<sup>2</sup> by using full-matrix least-squares methods. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were found on the residual density map and refined with isotropic thermal parameters without any restrictions. An absorption correction was applied via SADABS.<sup>9</sup> All calculations were performed with the Bruker SHELXTL (v. 6.10) package.<sup>10</sup> Crystal data (Table S1), atomic coordinates (Table S2), and interatomic distances and angles (Tables S4–S7) are summarized in the Supporting Information.

**Powder Characterization.** Polycrystalline powders were analyzed via powder X-ray diffraction (Rigaku Ultima-IV, Cu Kα radiation). The diffraction patterns were obtained in the range from 5 to 55° (2θ) with a scan speed of 2°/min and step size of 0.02°. Fourier transform infrared spectra were collected on a Nicolet 5PC spectrometer. The spectra were constructed by averaging 1024 scans from 400 to 4500 cm<sup>-1</sup> with a resolution of 0.241 cm<sup>-1</sup>. Electron probe microanalysis data were collected from pressed-powder disks with a Cemeica SX-50 system. Characteristics X-ray intensities were collected with wavelength dispersive spectrometers and gas-flow proportional detectors from 20 random spots on the sample; Zn metal and ScPO<sub>4</sub> were used as standards.

**Computational Methods.** Four molecular Sc dimer complexes were created from the crystal structure to capture the chemical environment found in the crystal array (Figure 2): [3Sc<sub>2</sub>•8NO<sub>3</sub>]<sup>2-</sup>, [4Sc<sub>2</sub>•2NO<sub>3</sub>]<sup>6+</sup>, [Sc<sub>2</sub>•2NO<sub>3</sub>]<sup>0</sup>, and [Sc<sub>2</sub>]<sup>2+</sup> (Supporting Information, pp S11–S14). The geometries and vibrational spectra were computed at the HF/6-31G(d,p) level of theory with IEFPCM-UFF continuum solvation model for water.<sup>11,12</sup> Geometry optimizations with solvation corrections resulted in molecular geometries more similar to the crystal array than those obtained from gas phase geometry optimizations (RMSD 0.3537 and 0.4841 Å, respectively).

**Least-Squares Fitting Procedure.** To identify the individual IR vibrational modes that constitute each of the peaks in the FTIR spectrum of [Sc<sub>2</sub>(μ-OH)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>, a Least-Squares Fitted Computed IR (LSFC-IR) spectrum was created from the

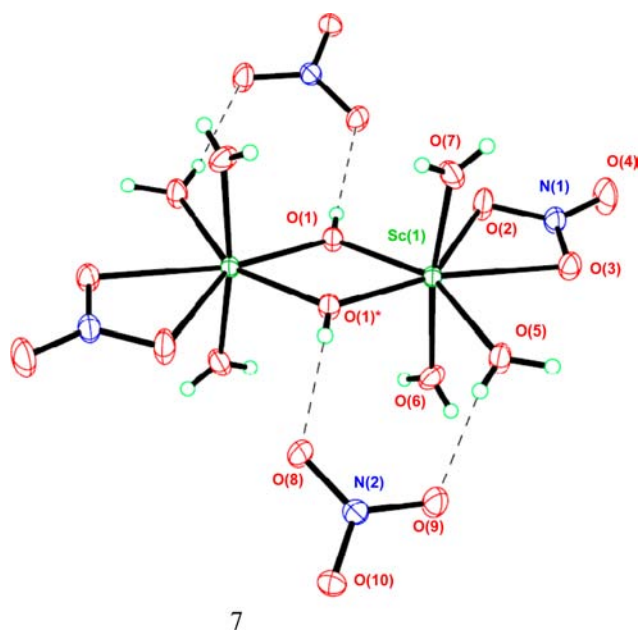
computed frequencies and IR intensities. The procedure is as follows: (i) Each computed IR vibrational mode was mathematically described with a Gaussian function generated from the computed IR vibrational frequency and intensity. Two global scaling parameters were introduced for the modulation of frequency (*F*) and amplitude (*A*) for each computed structure. In addition, we introduced individual scaling parameters (*W<sub>i</sub>*) for the width of each Gaussian. (ii) The parameters (*F*, *A*, and *W<sub>i</sub>*) were iterated to minimize the root-mean-square deviation (RSMD) between the trial LSFC-IR and the experimental spectrum. We removed Gaussians that (a) were redundant vibrational modes found in several computed species and (b) evolved to vanishingly small IR intensities. The vibrational modes of all eliminated peaks were checked and verified manually for chemical relevance and redundancy. (iii) Minimization of the RMSD to a suitable convergence criteria results in the final LSFC-IR spectrum. The juxtaposition of the LSFC-IR spectrum to the experimental FT-IR spectrum enables the association of all the IR peaks with specific vibrational normal modes.

## RESULTS AND DISCUSSION

In a previous contribution,<sup>13</sup> we described a method for the synthesis of the “flat” Al<sub>13</sub> cluster [Al<sub>13</sub>(μ<sub>3</sub>-OH)<sub>6</sub>(μ-OH)<sub>18</sub>(H<sub>2</sub>O)<sub>24</sub>]<sup>15+</sup> from an aqueous solution of Al(NO<sub>3</sub>)<sub>3</sub>. The method entails the use of zinc metal as a reductant for HNO<sub>3</sub>(aq), which results in a controlled increase in the pH of the solution coincident with the dissolution of zinc. This rise in pH drives hydrolysis and condensation of aqueous Al<sup>3+</sup> species. Here, we have used the same method to force condensation of aqueous Sc<sup>3+</sup> species. A solution of 1.0 M Sc(NO<sub>3</sub>)<sub>3</sub>(aq) has a pH of 0.68. On addition of 0.375 mol equivalents of zinc, the metal slowly dissolves, and the pH gradually rises to 3.10 coincident with complete dissolution. Evaporation of water leads to preferential growth of single crystals of [Sc<sub>2</sub>(μ-OH)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>, which can readily be harvested. Alternatively, water can be fully evaporated at room temperature, producing a mixture of scandium hydroxide nitrate and Zn(NO<sub>3</sub>)<sub>2</sub>. Subsequent selective dissolution of Zn(NO<sub>3</sub>)<sub>2</sub> in isopropanol affords isolation of [Sc<sub>2</sub>(μ-OH)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> powder in 65% yield.

Structural analysis of the salt reveals the formation of a centrosymmetric dimer unit, cf., Figure 1. Each Sc atom occupies an environment of seven O atoms distributed among three aqua, two hydroxo, and one bis-ligated nitrate group. The environment is best described as a distorted pentagonal bipyramid with atoms O(1), O(1)\*, O(2), O(3), and O(5) defining the equatorial plane and atoms O(6) and O(7) occupying the axial positions. The six atoms Sc(1), O(2), O(3), N(1), O(4), and O(5) deviate from a common plane by less than 0.009 Å, forming a dihedral angle of 12.1° with the plane of atoms Sc(1), O(1), O(1)\*. The hydroxo groups bridge the Sc-centered polyhedra. Additional nitrate groups centered at atoms N(2) are connected to the dimer by hydrogen bonding through the hydroxo and an aqua ligand O(5).

Sc–O distances cover a range from 2.0515(12) to 2.3269(11) Å (Table 1). The distances become longer in the ligand order of hydroxo, aqua, and nitrate, reflecting the decreasing basicity of the O atoms. Two slightly different Sc–O(1) distances, 2.0729(12) Å and 2.0515(12) Å, result from the asymmetric disposition of the N(2) nitrate groups across the dimer. It should be noted, as demonstrated in Figure 2, that the nitrate groups participate in the formation of a three-dimensional hydrogen-bonding framework. Each unit cell contains four [Sc<sub>2</sub>(μ-OH)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>(NO<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> dimers and two nonligating nitrate groups centered by atoms N(2). The N(2)

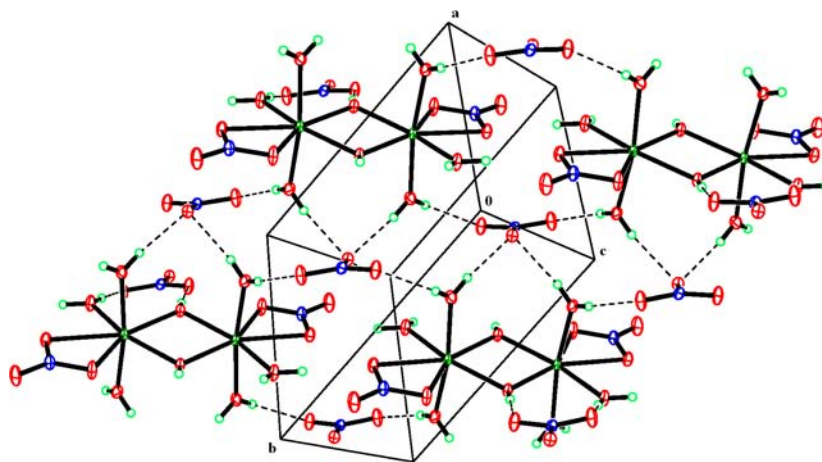


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**Figure 1.** A fragment of crystal structure of  $[\text{Sc}_2(\mu\text{-OH})_2(\text{H}_2\text{O})_6(\text{NO}_3)_2](\text{NO}_3)_2$ . Hydrogen bonds are shown by dashed lines.

**Table 1. Selected Interatomic Distances and Angles for  $[\text{Sc}_2(\mu\text{-OH})_2(\text{H}_2\text{O})_6(\text{NO}_3)_2](\text{NO}_3)_2$**

distances (Å)			
Sc(1)–O(1)	2.0729(12)	Sc(1)–O(1)*	2.0515(12)
Sc(1)–O(2)	2.2679(12)	Sc(1)–O(3)	2.3269(11)
Sc(1)–O(5)	2.1823(12)	Sc(1)–O(6)	2.1164(12)
Sc(1)–O(7)	2.1210(12)		
angles (deg)			
O(1)Sc(1)O(1)*	72.48(5)	O(1)Sc(1)O(2)	76.93(5)
O(2)Sc(1)O(3)	55.58(4)	O(3)Sc(1)O(5)	72.65(4)
O(5)Sc(1)O(1)*	83.75(5)	O(6)Sc(1)O(1)	88.56(5)
O(6)Sc(1)O(1)*	96.51(5)	O(6)Sc(1)O(2)	92.95(5)
O(6)Sc(1)O(3)	87.36(5)	O(6)Sc(1)O(5)	82.79(5)
O(6)Sc(1)O(7)	171.37(5)	O(7)Sc(1)O(1)	99.89(5)
O(7)Sc(1)O(1)*	87.81(5)	O(7)Sc(1)O(2)	87.29(5)
O(7)Sc(1)O(3)	85.66(5)	O(7)Sc(1)O(5)	90.28(5)

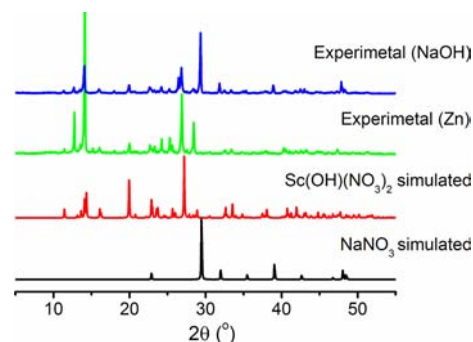


**Figure 2.** Packing of  $[\text{Sc}_2(\mu\text{-OH})_2(\text{H}_2\text{O})_6(\text{NO}_3)_2]^{2+}$  dimers in the crystal structure. Dashed lines represent hydrogen bonding. See Figure 1 caption for color code.

nitrate group is involved in hydrogen bonding with both  $\mu\text{-OH}$  and  $\eta\text{-H}_2\text{O}$ . The  $\text{O}\cdots\text{H}$  distances for these interactions range from 1.95(3) to 2.62(2) Å (Table S7, Supporting Information). While the hydrogen bonding network of the title compound differs markedly from that observed in  $[\text{Sc}_2(\text{NO}_3)_2(\text{H}_2\text{O})_6(\text{OH})_2](\text{NO}_3)_2 \cdot 12\text{-crown-4}$ , it has little effect on producing significant differences in the core dimer structures. Sc–O distances, for example, between the title compound and the 12-crown-4 derivative, differ by no more than 0.04 Å.

The structure determination provides additional insight into aqueous Sc chemistry. On the basis of  $^1\text{H}$  nuclear magnetic resonance studies, an average aqua–ligand coordination number of 3.9–5.1 in scandium(III) nitrate solutions has been suggested, even in the presence of perchloric acid.<sup>14</sup> This unusually low hydration number has been directly correlated to nitrate coordination in the first hydration sphere. Kanno and co-workers have suggested that the major species in an acidic nitrate solution is  $\text{Sc}(\text{NO}_3)_2^{2+}(\text{aq})$  with nitrate bis-ligated to Sc, which is also observed in the dimer of the crystal structure.<sup>15</sup>

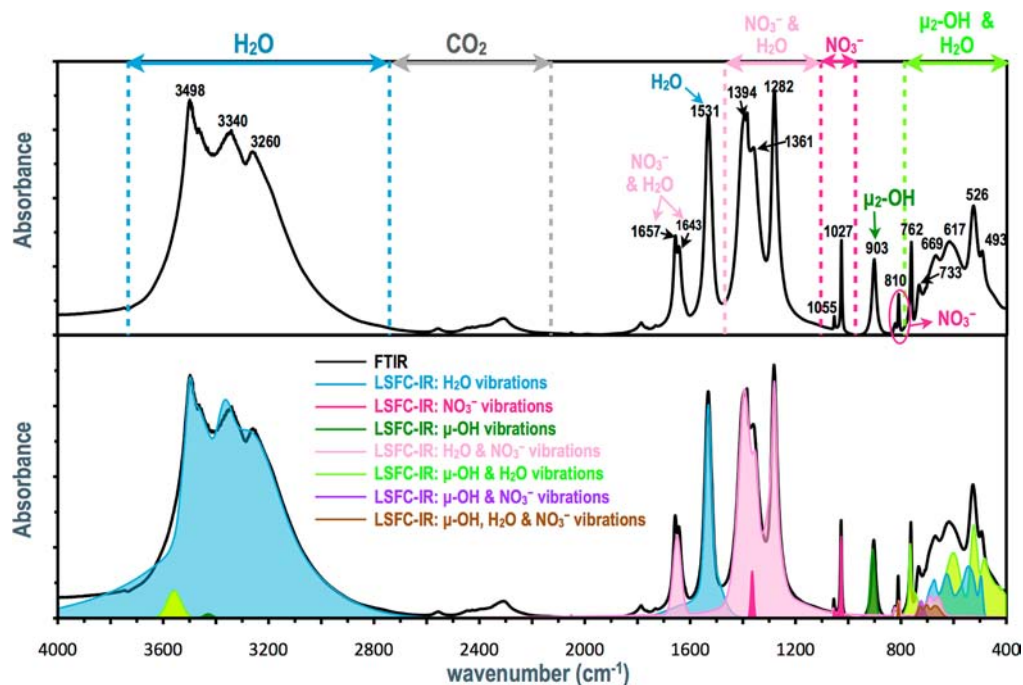
Representative X-ray diffraction patterns of the Sc products are shown in Figure 3. The pattern resulting from the Zn



**Figure 3.** Powder X-ray diffraction patterns.

synthesis method agrees well with the diffraction pattern simulated from the single crystal data of  $[\text{Sc}_2(\mu\text{-OH})_2(\text{H}_2\text{O})_6(\text{NO}_3)_2](\text{NO}_3)_2$ . As electron probe microanalysis reveals a Zn:Sc atomic ratio of 0.004:1 in the final product; hence, the washing procedure provides an effective means to remove the byproduct  $\text{Zn}(\text{NO}_3)_2$ . The diffraction pattern of the





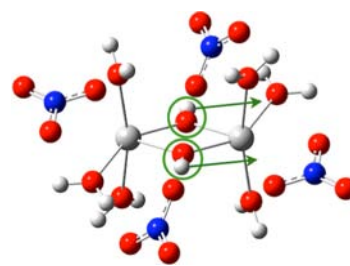
**Figure 4.** IR vibrations of the signature peaks (top) are shown with the LSFC-IR spectra that depict the contributions of each type of vibrational modes (bottom).

sample produced from controlled addition of NaOH(aq) is also shown. This pattern reveals a mixture of NaNO<sub>3</sub> and [Sc<sub>2</sub>(μ-OH)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>. We have not yet identified an effective solvent for selective removal of NaNO<sub>3</sub> from the mixture, but such a solvent should provide an efficient way to isolate the target compound in high yield.

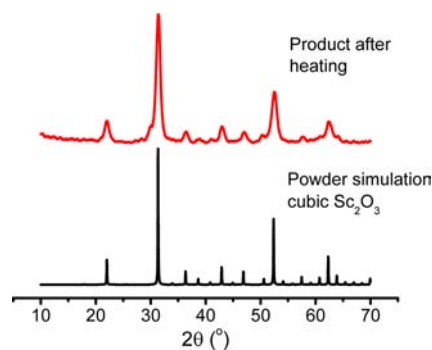
[Sc<sub>2</sub>(μ-OH)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> can be synthesized from Sc(NO<sub>3</sub>)<sub>3</sub>(aq) solutions on addition of either Zn or NaOH. This behavior differs from that of Al(NO<sub>3</sub>)<sub>3</sub>(aq), where different cluster species are isolated on the basis of the pathway to higher pH. A gradual rise in pH leads to the formation of the “flat” Al<sub>13</sub> hydroxide cluster, whereas titration with NaOH(aq) produces the Keggin Al<sub>13</sub> structure. For scandium, rapid ligand-exchange kinetics and the likely absence of a significant change in coordination number at high pH make product formation independent of reaction pathway.

The absorbance FTIR spectrum for a polycrystalline [Sc<sub>2</sub>(μ-OH)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> sample, associated LSFC-IR spectrum, and constituent vibrational normal modes are shown in Figure 4. The LSFC-IR spectrum is composed of 78 unique vibrational modes with a RMSD error of 0.0376 (RMSD is defined in the Supporting Information, p S17). The peak at 903 cm<sup>-1</sup> is a defining feature in the spectrum, comprising exclusively the μ-OH vibrations (mode *n* = 74, shown in Figure 5). The specific displacement vectors of important vibrational modes and overall peak assignments are given in the Supporting Information (p S18–S32).

On heating in air at temperatures above 450 °C, the title compound can be converted to Sc<sub>2</sub>O<sub>3</sub> (see X-ray diffraction patterns in Figure 6). The transformation temperature is largely dictated by the decomposition and elimination of nitrate. We have found that annealing powders under steam can effectively remove nitrate at lower temperatures (*T* < 250 °C). Under these conditions, nitrate likely leaves as an HNO<sub>3</sub>–H<sub>2</sub>O azeotrope, resulting in the formation of ScOOH, which then dehydrates to Sc<sub>2</sub>O<sub>3</sub>. The details of these processes as well as



**Figure 5.** Displacement vectors of the computed IR vibrational mode *n* = 74.



**Figure 6.** X-ray diffraction pattern of thermal decomposition product of [Sc<sub>2</sub>(μ-OH)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> after heating to 600 °C.

the use of the title compound for preparation of high-quality Sc<sub>2</sub>O<sub>3</sub> thin films will be described in a forthcoming contribution.

## CONCLUSIONS

A simple aqueous synthesis of [Sc<sub>2</sub>(μ-OH)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> has been developed for the production of gram-scale quantities of material. Structural analysis has revealed

condensation and nitrate binding modes. FTIR spectroscopy in conjunction with computational modeling has provided a detailed description of the vibrational spectrum and identification of unique vibrational modes. Controlled thermal decomposition of polycrystalline samples provides selective pathways for the formation of  $\text{Sc}_2\text{O}_3$  that can be altered by effectively controlling annealing conditions. We have clarified the fundamental aqueous chemistry of scandium in a pH regime preceding precipitation, and we have created a new approach for production of  $\text{Sc}_2\text{O}_3$  from a very simple aqueous precursor.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Crystallographic data, structural data, computational methods and data, and mass spectrometry data. 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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