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The Syntheses and Crystal Structures of Two Novel Aluminum Selenites, $Al_2(SeO_3)_3 \cdot 6H_2O$ and $AlH(SeO_3)_2 \cdot 2H_2O$

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$Al_2(SeO_3)_3 \cdot 6H_2O$ and $AlH(SeO_3)_2 \cdot 2H_2O$ were prepared hydrothermally at 70°C. $Al_2(SeO_3)_3 \cdot 6H_2O$ is trigonal (space group $P31c$) with $a = 8.8020(6)$ and $c = 10.7070(8)$ Å, $Z = 2$, $V = 718.39$ Å^3, 1377 observed reflections ($I > 3\sigma(I)$), $R = 3.27\%$, and $R_w = 3.55\%$. The structure consists of discrete $Al_2(SeO_3)_3 \cdot 6H_2O$ units which are linked via hydrogen bonding to form an open structure with channels running parallel to the [0001] direction. $AlH(SeO_3)_2 \cdot 2H_2O$ is monoclinic ($P2_1/n$) with $a = 7.3853(5)$, $b = 6.4895(6)$, and $c = 7.3958(7)$ Å, $\beta = 106.28(9)°$, $Z = 2$, $V = 340.24$ Å^3, 732 observed reflections, $R = 4.04\%$, and $R_w = 3.98\%$. The structure consists of octahedral AlO_6 units which are interlinked via the sharing of vertices with four separate selenite groups. The selenite groups form dimers which appear to contain a symmetry-restricted hydrogen bond. This symmetry-restricted bond is markedly shorter than the other hydrogen bonds in the structure. The infrared spectra and thermal decomposition behavior of both compounds are also reported.

Introduction

Structural studies of inorganic selenites have tended to concentrate on those of the first-row transition metals. For example, Kohn *et al.* synthesized the series of perovskite-related $M^{2+}SeO_3$ phases (M = Mg, Mn, Co, Ni, Cu, Zn) (*1*), Lieder and Gattow prepared the hydrated series $M^{2+}SeO_3 \cdot 2H_2O$ (M = Mn, Co, Ni, Zn) (*2*), and Effenberger prepared strontium copper selenites (*3*). The selenites of lanthanide ions, e.g., $Ce(SeO_3)_2$ (*4*), $NaLa(SeO_3)_2$ (*5*), and $LnH(SeO_3)_2 \cdot 2H_2O$ (*6*), have also been recently prepared. The only structural information available on selenites of aluminum comes from infrared spectra (*7–9*). These papers report a number of different aluminium selenites, including $Al_2(SeO_3)_3 \cdot 6H_2O$ which was formulated as consisting of the aqua ion, $[Al(H_2O)_6]^{3+}$, linked via hydrogen bonding to an SeO_3^{2-} anion, as well as other phases prepared by hydrothermal and double decomposition reactions. This paper describes the low-temperature (e.g., 70°C) hydrothermal synthesis, crystal structure elucidation, TGA, and infrared spectra of two aluminium selenite hydrates, $Al_2(SeO_3)_3 \cdot 6H_2O$ and $AlH(SeO_3)_2 \cdot 2H_2O$.

Synthesis

The title compounds were prepared hydrothermally from mixtures of $Al(NO_3)_3 \cdot 9H_2O$ and H_2SeO_3 in polypropylene bottles.

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TABLE I

CRYSTAL DATA AND DETAILS OF DATA COLLECTION AND STRUCTURE ANALYSES

	Molecular formula	
	$Al_2(SeO_3)_3 \cdot 6H_2O$	$AlH(SeO_3)_2 \cdot 2H_2O$
Formula weight	542.7	317.8
Crystal size (mm)	0.5 × 0.2 × 0.2	0.4 × 0.3 × 0.1
Crystal system	Trigonal	Monoclinic
a (Å)	8.8020(6)	7.3853(5)
b (Å)	8.8020(6)	6.4895(6)
c (Å)	10.7070(8)	7.3958(7)
α (°)	90	90
β (°)	90	106.28(9)
γ (°)	120	90
V (Å^3)	718.39	340.24
Space group	$P31c$ (No. 159)	$P2_1/n$ (No. 14)
D_c (g cm^{-3})	2.468	3.054
$F(000)$	520	294
Z	2	2
Linear absorption coefficient (cm^{-1})	77.894	108.83
X radiation	Mo$K\alpha$	Mo$K\alpha$
2θ min, max (°)	1, 65	1, 60
Observed data	1377	732
$[I > n\sigma(I)]$ $n =$	3	3
Absorption correction min, max	1.56, 2.63	1.79, 3.90
Min h,k,l	−6, −1, −14	−10, −1, −1
Max h,k,l	6, 12, 14	10, 9, 10
No. of parameters	71	58
Weighting scheme		
Coefficients	17.477, −8.847, 9.005	4.06, −2.83, 2.18, −1.62
$\Delta\rho$ (e Å^{-3})	2.90	0.17
Final shift/error	0.001	0.015
Final R	3.27	4.04
Final R_w	3.55	3.98

Tetramethyl ammonium hydroxide was added to a solution of the nitrate to produce a suspension of aluminium hydroxide. To these mixtures, selenous acid (2 *M*) was added dropwise until the required pH value for the reaction was reached. One reaction was conducted at a pH of approximately 3 while the other was at a pH of approximately 8. The two bottles were heated at 70°C for 10 days and then left to cool. Colorless hexagonal prismatic crystals of $Al_2(SeO_3)_3 \cdot 6H_2O$ (I) were recovered from the approximately neutral reaction mixture, and colorless "brick-like" crystals of $AlH(SeO_3)_2 \cdot 2H_2O$ (II) were recovered from the acidic mixture. The infrared spectra for the two compounds were obtained on a Perkin–Elmer spectrometer. Thermogravimetric analyses were carried out on a DuPont 9900 system using a heating rate of 10°/min in air.

Structure Determination

Suitable single crystals for structure determination were selected for each of the

TABLE II

FINAL ATOMIC COORDINATES AND THERMAL PARAMETERS FOR $Al_2(SeO_3)_3 \cdot 6H_2O$

Atom	x/a	y/b	z/c	U(iso)	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Se(1)	0.25739(5)	0.87557(5)	0.337(2)	0.0134	0.0136(2)	0.0122(2)	0.0151(2)	−0.0001(1)	−0.0001(1)	0.0067(1)
Al(1)	0.3333	0.6667	0.110(2)	0.0135	0.0129(6)	0.0129(6)	0.0147(9)	0.0000	0.0000	0.0064(3)
Al(2)	0.3333	0.6667	0.543(2)	0.0134	0.0127(6)	0.0127(6)	0.0148(9)	0.0000	0.0000	0.0064(3)
O(1)	0.3790(4)	0.8656(4)	0.205(2)	0.0170	0.022(2)	0.014(1)	0.019(1)	−0.002(1)	0.004(1)	0.010(1)
O(2)	0.5172(4)	0.8328(5)	0.006(2)	0.0191	0.019(2)	0.017(1)	0.023(1)	0.001(1)	0.006(1)	0.009(1)
O(3)	0.3243(4)	0.0885(4)	0.327(2)	0.0189	0.034(1)	0.014(1)	0.018(1)	0.000(1)	0.001(2)	0.014(1)
O(4)	0.3786(4)	0.8657(4)	0.449(2)	0.0177	0.023(2)	0.015(1)	0.018(1)	0.002(1)	−0.004(1)	0.010(1)
O(5)	0.5177(4)	0.8331(5)	0.648(2)	0.0187	0.020(2)	0.017(1)	0.021(1)	−0.002(1)	−0.007(1)	0.009(1)
H(1)	0.418(9)	0.81(1)	0.960(7)	0.02(2)						
H(2)	0.48(2)	0.40(2)	0.49(1)	0.08(5)						
H(3)	0.43(1)	0.24(2)	0.21(1)	0.06(3)						
H(4)	0.60(2)	0.08(2)	0.17(1)	0.12(5)						

two phases and mounted on thin glass fibers using "superglue." Room temperature intensity data were collected on compound I on a Huber automated four-circle diffractometer (graphite-monochromated Mo$K\alpha$ radiation, λ = 0.71069 Å) as outlined in Table I. Twenty reflections were located and centered by searching reciprocal space and indexed to obtain a unit cell and orientation matrix. Unit cell constants were optimized by least-squares refinement, resulting in the lattice parameters shown in Table I. Data were collected in the $\omega - 2\theta$ scanning mode. Three standard reflections were monitored during the course of the experiment and these showed no significant intensity variation. The scan speed was 6° min^{-1} with a scan range of 1.3° below $K\alpha_1$ to 1.6° above $K\alpha_2$. Psi-scans for three selected reflections were used to correct for crystal absorption. The raw data were reduced using a Lehmann–Larsen profile fitting routine and the normal corrections for Lorentz and polarization effects applied. All the data collection and reduction routines were based on the UCLA package.

The systematic absences (000l: $l \neq 2n$

TABLE III

BOND DISTANCES (Å) AND ANGLES (°) FOR $Al_2(SeO_3)_3 \cdot 6H_2O$

Se(1)–O(1)	1.716(3)	Se(1)–O(3)	1.660(3)
Se(1)–O(4)	1.716(3)		
Al(1)–O(1)	1.887(3) × 3	Al(1)–O(2)	1.908(4) × 3
Al(2)–O(4)	1.885(3) × 3	Al(2)–O(5)	1.911(4) × 3
O(2)–H(1)	0.84(8)	O(2)–H(2)	0.8(2)
O(5)–H(4)	0.8(2)	O(5)–H(3)	0.9(1)
O(3)–H(1)	1.80(8)	O(3)–H(3)	1.7(1)
O(1)–H(4)	1.9(2)	O(4)–H(2)	1.9(2)
O(3)–Se(1)–O(1)	100.2(2)	O(4)–Se(1)–O(1)	99.0(2)
O(4)–Se(1)–O(3)	100.4(2)		
O(1)–Al(1)–O(1)	93.7(2)	O(2)–Al(1)–O(1)	84.2(1)
O(2)–Al(1)–O(1)	172.9(2)	O(2)–Al(1)–O(1)	93.2(2)
O(2)–Al(1)–O(2)	89.2(2)		
O(4)–Al(2)–O(4)	93.9(2)	O(5)–Al(2)–O(4)	84.1(1)
O(5)–Al(2)–O(4)	93.0(2)	O(5)–Al(2)–O(5)	89.3(2)
O(5)–Al(2)–O(4)	173.0(2)		

TABLE IV

Final Atomic Coordinates and Thermal Parameters for $AlH(SeO_3)_2 \cdot 2H_2O$

Atom	x/a	y/b	z/c	U(iso)	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Se(1)	0.40673(8)	0.19416(8)	0.65478(7)	0.0086	0.0121(2)	0.0093(2)	0.0052(2)	−0.0003(2)	0.0009(2)	0.0001(2)
Al(1)	0.5000	0.5000	1.0000	0.0083	0.014(1)	0.010(1)	0.0042(9)	0.0006(8)	0.0016(8)	0.0010(9)
O(1)	0.4629(5)	0.6890(7)	0.4776(5)	0.0130	0.014(2)	0.018(2)	0.009(2)	−0.000(2)	0.004(1)	−0.002(2)
O(2)	0.9143(7)	0.2247(8)	0.6290(6)	0.0152	0.017(2)	0.019(2)	0.011(2)	−0.001(2)	0.004(2)	0.002(2)
O(3)	0.8518(6)	0.1017(7)	0.2700(6)	0.0105	0.014(2)	0.017(2)	0.009(2)	0.008(2)	−0.001(1)	−0.002(2)
O(4)	0.7037(6)	0.3372(7)	−0.0166(5)	0.0117	0.014(2)	0.017(2)	0.008(2)	−0.002(2)	0.002(1)	0.005(2)
H(1)	0.80(2)	0.24(2)	0.61(1)	0.05						
H(2)	0.56(1)	0.71(2)	0.78(1)	0.05						

absent, $hh\overline{2h}l$: $l \neq 2n$) were consistent with the space groups $P\bar{3}1c$, $P31c$ in the trigonal system, and hexagonal $P6_3mc$, $P\bar{6}2c$, and $P6_3/mmc$. Measurement of the second-harmonic generation indicated that the compound had a noncentrosymmetric structure (SHG approximately equal to that of quartz), and inspection of selected equivalent reflections indicated that the space group was $P31c$. The structure was solved by a combination of direct methods and Fourier syntheses: the selenium and aluminium atom positions were found using the direct methods program SHELXS86 (*10*) and the oxygen atom positions were located from Fourier difference syntheses following least-squares refinement of the known atom positions. The two hydrogen atoms of one of the water molecules were found from further difference Fourier syntheses, but these syntheses did not reveal the positions of the hydrogen atoms on the other water molecule. However, by inspection of the hydrogen bonding involving the known hydrogen atoms it was possible to predict the positions of the final atoms; these were then placed in their calculated locations and refined successfully. Final full-matrix refinements were against F and included anisotropic temperature factors for Se, Al, and O, and isotropic temperature factors for the hydrogens. The Flack enantiopole parameter (*11*) refined to 0.91(4), and this revealed that the original model was of the wrong hand. The correct transformation of the atomic

TABLE V

Bond Distances (Å) and Angles (°) for $AlH(SeO_3)_2 \cdot 2H_2O$

Se(1)–O(1)	1.729(4)	Se(1)–O(3)	1.685(4)
Se(1)–O(4)	1.682(4)		
Al(1)–O(2)	1.943(5) × 2	Al(1)–O(4)	1.871(4) × 2
Al(1)–O(3)	1.866(4) × 2		
O(1)–H(1)	1.9(1)	O(1)–H(2)	2.1(1)
O(2)–H(1)	0.8(1)	O(2)–H(2)	0.7(1)
O(3)–Se(1)–O(1)	101.1(2)	O(4)–Se(1)–O(1)	98.4(2)
O(4)–Se(1)–O(3)	100.7(2)		
O(2)–Al(1)–O(2)	180.0	O(3)–Al(1)–O(3)	180.0
O(3)–Al(1)–O(2)	90.4(2)	O(3)–Al(1)–O(2)	89.6(2)
O(4)–Al(1)–O(2)	90.7(2)	O(4)–Al(1)–O(2)	89.3(2)
O(4)–Al(1)–O(3)	89.0(2)	O(4)–Al(1)–O(3)	91.0(2)
O(4)–Al(1)–O(4)	180.0		

coordinates was then applied. The origin was fixed as the centroid of the structure (*12*), and the weighting scheme was that of Tukey and Prince, fitted using a modified Chebyshev polynomial.

The intensity data for compound II were collected on an Enraf–Nonius CAD4 diffractometer (graphite monochromated Mo$K\alpha$ radiation, $\lambda = 0.71069$ Å, room temperature). The orthorhombic unit cell constants were determined from the positions of 25 centered reflections and refined to the final values given in Table I. Data were collected using the $\bar{\omega} - 2\theta$ scanning mode with a scan width of $(0.8 + 0.35 \tan \theta)°$. Three standard reflections were monitored for orientation change and intensity variation and these showed no significant trends during the course of the experiment. Psi-scan data on three reflections ($\chi > 80°$) were recorded to apply an empirical absorption correction. The raw data were prepared for structure solution and refinement using the program RC85 (*13*).

The systematic absences ($0k0$; $k \neq 2n$ absent, $h0l$: $h + l \neq 2n$) were consistent with the space group $P2_1/n$. The selenium atom positions were located using the direct methods program SHELXS86, and subsequent Fourier syntheses revealed the locations of the aluminium and oxygen atoms, as well as the protons from the water molecule. For the final cycle of least-squares refinement against F, a Tukey–Prince weighting scheme was applied.

All least-squares, Fourier, and subsidiary calculations were carried out using the Oxford CRYSTALS system (*14*), running on a VAX 3800 computer. Complex neutral atom scattering factors were obtained from the International Tables, Vol. IV (*15*).

Discussion

Final atomic coordinates, thermal parameters, and bond distances and angles are given in Tables II, III, IV, and V. The neutral and acidic conditions under which the compounds were prepared produced the expected octahedral coordination of oxygen about aluminium, and the more acidic reaction producing protonated selenite groups.

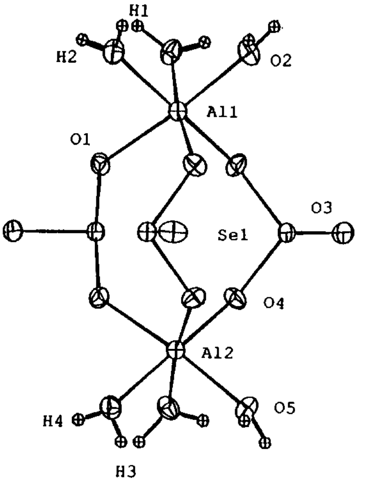

FIG. 1. The molecular unit present in $Al_2(SeO_3)_3 \cdot 6H_2O$.

$Al_2(SeO_3)_3 \cdot 6H_2O$ contains almost regular octahedral aluminium (av Al(1)–O distance = 1.898(4) Å, av Al(2)–0 distance = 1.899(4) Å, O–Al–O angles ranging from 84.1(1)° to 93.1(2)°), and trigonal pyramidal SeO_3 groups with bond distances and angles in close agreement with those reported for similar compounds (*1–3*). The structure consists of molecular units of formula $Al_2(SeO_3)_3 \cdot 6H_2O$, which are interconnected only via hydrogen bonds. These molecular units contain both Al(1) and Al(2) which are linked via the sharing of the non-water oxygens, O(1) and O(4), and Se(1) to produce a trigonal-prismatic cavity directly between the two aluminium atoms, as shown in Fig. 1. The molecular units are completed by the water molecules (containing O(2) and O(5)). Hydrogen bonding through these water molecules between the "molecules" occurs in such a way as to produce channels in the structure parallel with [0001] (Fig. 2). The final Fourier difference syntheses revealed

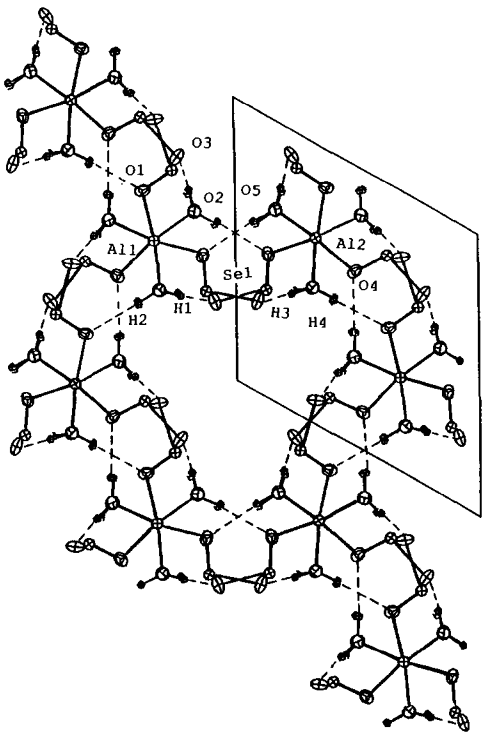

FIG. 2. $Al_2(SeO_3)_3 \cdot 6H_2O$ viewed in the [0001] direction. Hydrogen bonds are shown as dotted lines.

fairly large (2.9 e Å^{-3}) residual electron density peaks in positions close to the center of these channels, but they could not be refined as any atoms, and there is no other evidence (e.g., from the TGA) to indicate the presence of any other species in the structure. The molecular units are oriented so that their Al(1)–Al(2) axis is parallel to the c-axis. The hydrogen bonding in the system is quite complex, involving all the oxygens in the structure. Each water molecule (H(1)–O(2)–H(2) and H(3)–O(5)–O(4)) has one proton, (H(1) and H(3), respectively) which is hydrogen bonded to O(3) in a selenite unit. Each of the water molecules in the same molecular unit is bound to a different unit. The remaining hydrogen atoms are hydrogen bonded to the other non-water oxygens to form O(2)–H(2) ··· O(4) and O(5)–H(4) ··· O(1) linkages. This system of hydrogen bonding is illustrated in Fig 3. TGA showed a steady weight loss, corresponding to the loss of 6 mole of water, at about 190°C, followed by loss of SeO_2 to leave a residual solid, which from the observed weight loss could be formulated as Al_4SeO_8 (observed weight loss = 72%, calculated = 71%). This residual powder was found to be amorphous by powder X-ray diffraction.

$AlH(SeO_3)_2 \cdot 2H_2O$ also contains regular aluminium coordination (av Al–O distance = 1.890(5) Å, O–Al–O angle range 89.0(2)° to 90.9(2)°). The structure contains discrete $AlO_4(OH_2)_2$ octahedra which share their four non-water vertices with four selenite groups to form a fairly open structure in which there are small channels running par-

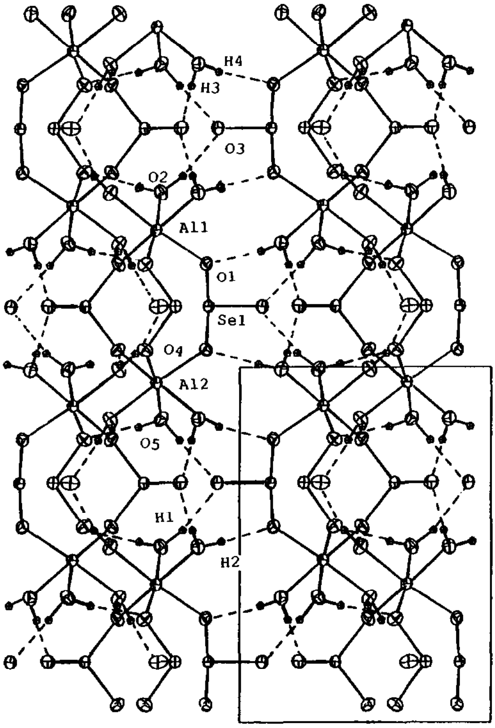

FIG. 3. Projection of $Al_2(SeO_3)_3 \cdot 6H_2O$ in the [1$\bar{2}$10] direction.

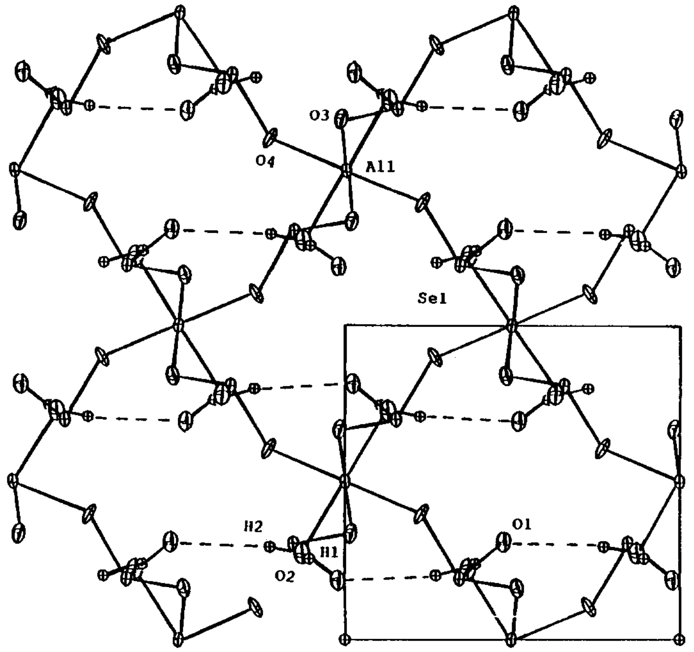

FIG. 4. $AlH(SeO_3)_2 \cdot 2H_2O$ viewed in the [001] direction.

allel to [001]. A projection of the structure in the [001] direction is illustrated in Fig. 4 and a view down the [010] direction is shown in Fig. 5. The final hydrogen atom in the structure could not be found by difference Fourier methods, but an analysis of the infrared spectrum reveals no evidence for two distinct types of selenite group. Such a result indicates that the final proton is shared between two selenite groups to form a (SeO_3HSeO_3) dimer. The IR spectrum (Fig. 6 and Table VI) is similar to that given in the literature for $GaH(SeO_3)_2 \cdot 2H_2O$ (7). Unfortunately, the location of the final hydrogen atom could not be found from the X-ray data, and thus it could not be decided whether it is (a) located at the center of symmetry (coordinates 0,0,0) of the structure, building a linear symmetric hydrogen bond, (b) statistically distributed between two half-occupied positions correlated by the center of symmetry, or (c) a normal hy-

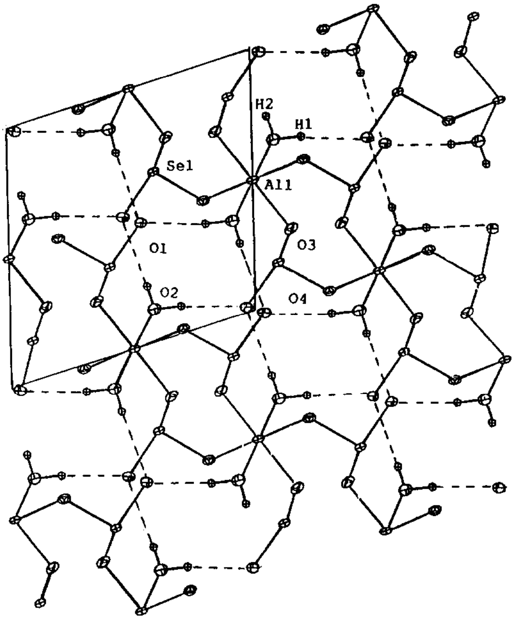

FIG. 5. $AlH(SeO_3)_2 \cdot 2H_2O$ viewed in the [010] direction.

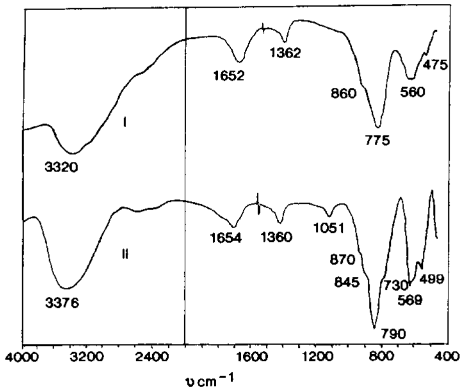

FIG. 6. The IR spectra of $Al_2(SeO_3)_3 \cdot 6H_2O$ (I) and $AlH(SeO_3)_2 \cdot 2H_2O$ (II).

drogen bond which would require the lowering of the space group symmetry to $P2_1$. However, a splitting of the selenite groups into SeO_3 and $SeO_2(OH)$ would cause a definitely longer Se–(OH) distance than that of Se–O. Refinement in $P2_1/n$ instead of $P2_1$ would therefore result in an "average" bond length and a high anisotropic motion for the oxygen in question (*16*). This is not in fact the case here, and it therefore seems more likely that the hydrogen is located at the center of symmetry, as in (a). In crystal structures studied by neutron diffraction, all three cases are known. For example, in $K_3Na(H_2P_2O_7)_2$ (*17*) there is a symmetric hydrogen bond as well as a hydrogen atom that is disordered over two separate sites restricted by a twofold axis. In $CaHPO_4$ (*18*), however, there is a symmetric hydrogen bond at room temperature, with the hydrogen atom centered on a center of symmetry, while at low temperatures a phase transition occurs such that the symmetry restriction on this bond is lost and a normal ordered hydrogen bond is found. The O(1)–O(1) hydrogen bond distance (2.514(9) Å) in II is markedly shorter than the other two hydrogen bonding distances in this structure (O(1) ··· H(1)–O(2) = 2.733(6) Å and O(1) ··· H(2)–O(2) = 2.804(6) Å), in agreement with anomalously short distances found for other structures with symmetry-restricted hydrogen bonds (*19*). The TGA showed loss of 2 mole of water at about 250°C, followed by a further weight loss to a final compound which could also be formulated as Al_4SeO_8 (observed weight loss = 75%, calculated = 75%).

TABLE VI

THE BAND MAXIMA (υ cm⁻¹) AND ASSIGNMENTS OBTAINED FROM THE IR SPECTRA OF THE TWO COMPOUNDS

I $Al_2(SeO_3)_3 \cdot 6H_2O$		II $AlH(SeO_3)_2 \cdot 2H_2O$	
3320	$\upsilon(H_2O)$	3376	$\upsilon(H_2O)$
1652	$\delta(H_2O)$	1654	$\delta(H_2O)$
1362	$\delta(OH)$	1360	$\delta(OH)$
		1051	$\delta(SeO_2O\text{–}H)$
775	$\upsilon_3(SeO_3)$	730[a]	$\upsilon_3(SeO_3)$
		790	$\upsilon_3(SeO_3)$
		845[a]	$\upsilon_3(SeO_3)$
860[a]	$\upsilon_1(SeO_3)$	870[a]	$\upsilon_1(SeO_3)$
560	$\upsilon(AlO)$	569	$\upsilon(AlO)$
475	$\upsilon_2(SeO_3)$	499	$\upsilon_2(SeO_3)$

[a] These bands are shoulders.

Conclusion

These studies, combined with other works (*3–6*), have shown that hydrothermal synthesis is an excellent method of producing new selenite materials containing metals from all parts of the periodic table. The conditions of the reactions, especially the pH, are of vital importance in determining the final products, e.g., the aluminium coordination and the type of selenite ion produced, and variation of these conditions could lead to other new phases; e.g., a more alkaline reaction mixture may produce selenite compounds containing tetrahedral aluminium. Furthermore, there is obviously much scope for the preparation of gallium and iron analogues of the phases prepared here.

Acknowledgments

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