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Flux Synthesis, Crystal Structures, and Solid-State NMR Spectroscopy of Two Indium Silicates Containing Varied In–O Coordination Geometries

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Two novel indium silicates, $K_5In_3Si_7O_{21}$ (**1**) and $K_4In_2Si_8O_{21}$ (**2**), have been synthesized by a flux-growth method and characterized by single-crystal X-ray diffraction. The structure of **1** consists of siebener single chains of corner-sharing SiO_4 tetrahedra running along the *b* axis linked via corner-sharing by In_2O_9 face-sharing octahedral dimers and InO_5 trigonal bipyramids to form a 3D framework. The structure of **2** consists of a 3D silicate framework containing 6- and 14-ring channels. InO_5 square pyramids are located within the 14-ring channels sharing corners with the silicate framework. The solid-state ^{29}Si MAS NMR spectrum of compound **1** was recorded; it shows the influence of the indium atoms in the second coordination sphere of the silicon on the chemical shift. Crystal data: **1**, orthorhombic, $Pna2_1$ (No. 33), $a = 12.4914(3)$ Å, $b = 16.8849(3)$ Å, $c = 10.2275(2)$ Å, $V = 2157.1(1)$ Å^3 and $Z = 4$; **2**, monoclinic, $P2_1/n$ (No. 14), $a = 8.4041(3)$ Å, $b = 11.4919(4)$ Å, $c = 10.4841(3)$ Å, $\beta = 90.478(2)°$, $V = 1012.5(1)$ Å^3 and $Z = 2$.

Introduction

Metal silicates with microporous structures have attracted tremendous research interest because of their wide applications in separation, ion exchange, and catalysis.[1] Introduction of metals with different coordination geometries into the silicate frameworks enriches their structural chemistry and physical and chemical properties. A large number of silicates of transition metals,[2] main-group elements,[3] uranium,[4] and lanthanide elements[5] have been synthesized, and some of them showed good thermal stability, absorption, ion-exchange, and useful optical properties. We have been interested in the exploratory synthesis of mixed octahedral-tetrahedral frameworks and have obtained quite a few metal silicates via high-temperature high-pressure hydrothermal synthesis. For example, several indium silicates with dissimilar silicate structural types including 12-membered single rings, unbranched vierer 4-fold chains, and $CdSO_4$-topological-type frameworks were synthesized.[3b−d] All indium atoms

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in these compounds are octahedrally coordinated by oxygen atoms. A cobalt−indium silicate containing 20-membered-ring silicate single layers with a very low Si/O ratio was also synthesized.[6] Although a large number of aluminosilicates and gallosilicates have been synthesized, much less work has been reported on indium silicates. Indium represents an interesting case since, by comparison with the smaller Al and Ga, which usually adopt 4-fold coordination, In is expected to occur with octahedral coordination.

Metal silicates can also be synthesized using flux-growth methods. For example, emerald ($Be_3Al_2Si_6O_{18}$/Cr) crystals were grown by a flux evaporation method in the $K_2O−MoO_3$ system.[7] New scandium silicates with open-framework structures, $Cs_3ScSi_8O_{19}$ and $K_2ScFSi_4O_{10}$, were synthesized from alkali metal fluoride−MoO_3 fluxes.[8,9] In an attempt to explore whether we can synthesize new metal silicates using a flux-growth method, we obtained the first salt-inclusion stannosilicate that contains both Na^+ and F^- ions in the structural channels.[3e] As an extension of our research on the system of indium silicates, we report herein flux synthesis of two novel indium silicates which contain unusual coordination geometries of In−O polyhedra, such as In_2O_9 face-sharing octahedral dimers and InO_5 trigonal bipyramids in $K_5In_3Si_7O_{21}$ (denoted as **1**) and InO_5 square pyramids in $K_4In_2Si_8O_{21}$ (denoted as **2**). The solid-state NMR spectroscopy of **1** has also been studied.

Experimental Section

Synthesis. A mixture of 1.0 g of KF (Merck, >99%), 1.0 g of V_2O_5 (Merck, >99%), 0.139 g of In_2O_3 (Cerac, 99.8%), and 0.24 g of SiO_2 (Alfa Aesar, 99.995%) (mole ratio K/In/Si = 17.2:1:4) was placed in a 4 mL platinum crucible, heated to 750 °C at 50 °C h^{-1}, and isothermed for 24 h, followed by slow cooling to 450 °C at 5 °C h^{-1} and quenching to room temperature. The flux was dissolved with hot water, and the solid product was obtained by suction filtration. The product contained two kinds of colorless crystals. As indicated by single-crystal X-ray diffraction, the block crystals are $K_5In_3Si_7O_{21}$ (**1**), and the prismatic ones are $K_4In_2Si_8O_{21}$ (**2**). A single phase of **1** was obtained if the mole ratio of In/Si was changed to 3:7, according to the stoichiometry of the compound, and the quench temperature was raised to 725 °C. Its X-ray powder pattern (Figure S1 in Supporting Information) is in good agreement with the calculated pattern based on the results of single-crystal structure determination. The yield was 67% based on indium. As the quench temperature was lowered, crystal **2** crystallized along with crystal **1**. Many attempts to get a single phase of **2** have been made, but the products always contained two phases, namely **1** and **2**.

Single-Crystal X-ray Diffraction. Crystals of dimensions 0.2 × 0.2 × 0.25 mm^3 for **1** and 0.1 × 0.1 × 0.2 mm^3 for **2** were selected for indexing and intensity data collection on a Bruker APEX diffractometer equipped with a normal-focus 2 kW sealed-tube X-ray source. Intensity data were collected at room temperature in 1315 frames with ω scans (width 0.30° per frame), and the program SADABS was used for absorption correction ($T_{min/max}$ = 0.653/0.984 for **1**; 0.760/0.962 for **2**).[10] On the basis of reflection conditions, statistical analysis of the intensity distributions, and successful solution and refinement of the structures, the space group was determined to be $Pna2_1$ (No. 33) for **1** and $P2_1/n$ (No. 14) for **2**. The structures were solved by direct methods and difference Fourier syntheses. The final cycles of least-squares refinement including atomic coordinates and anisotropic thermal parameters for all atoms converged at R1 = 0.0188, wR2 = 0.0481 for **1** and R1 = 0.0191, wR2 = 0.0498 for **2**. The Flack x parameter for **1** was 0.00(1), indicative of a correct absolute structure. The final difference electron density maps were nearly featureless, and the highest peak and deepest hole were 0.75 and −1.25 e $Å^{-3}$ for **1** and 0.46 and −0.51 e $Å^{-3}$ for **2**. All calculations were performed using the SHELXTL, version 5.1, software package.[11] Crystallographic data for **1** and **2** are summarized in Table 1. Selected bond lengths and bond-valence sums for **1** and **2** are provided in Table 2.

Table 1. Crystallographic Data for $K_5In_3Si_7O_{21}$ (**1**) and $K_4In_2Si_8O_{21}$ (**2**)

	1	**2**
fw	1072.59	946.76
space group	$Pna2_1$ (No. 33)	$P2_1/n$ (No. 14)
a (Å)	12.4914(3)	8.4041(3)
b (Å)	16.8849(3)	11.4919(4)
c (Å)	10.2275(2)	10.4841(3)
β (deg)		90.478(2)
V ($Å^3$)	2157.14(8)	1012.51(6)
Z	4	2
T (°C)	23	23
λ(Mo Kα) (Å)	0.71073	0.71073
D_{calcd} (g cm^{-3})	3.303	3.105
μ(Mo Kα) (mm^{-1})	4.634	3.678
R1[a]	0.0188	0.0191
wR2[b]	0.0481	0.0498

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_{o2})^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o,0) + 2(F_c)^2]/3$, where $a = 0.0307$ and $b = 0.03$ for **1** and $a = 0.0228$ and $b = 0$ for **2**.

Solid-State NMR Measurements. Solid state ^{29}Si NMR experiments were performed on a Varian Infinityplus-500 spectrometer, equipped with a Chemagnetics 7.5 mm magic angle spinning (MAS) probe, with a resonance frequency of 99.3 MHz for the ^{29}Si nucleus. A pulse length of 2 μs (π/4 pulse) and a repetition time of 50 s were used to obtain ^{29}Si MAS NMR spectra. T_1 values of about 50 s for all the ^{29}Si resonances were obtained with an inversion−recovery pulse sequence. ^{29}Si chemical shifts were externally referenced to tetramethylsilane (TMS) at 0 ppm.

Results and Discussion

Structure. The asymmetric units of the title compounds are shown in Figure 1. The structure of **1** is constructed from the following structural elements: 5 potassium sites, 1 InO_5 trigonal bipyramid, 1 In_2O_9 face-sharing octahedral dimer, and 7 SiO_4 tetrahedra. All atoms are in general positions. The fundamental building units are single siebener chains of corner-sharing SiO_4 tetrahedra in a period of seven. As shown in Figure 2, adjacent silicate chains are interconnected via corner-sharing by In_2O_9 face-sharing octahedral dimers and InO_5 distorted trigonal bipyramids to form a 3D framework. It delimits two kinds of channels to accommodate

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Table 2. Selected Bond Lengths (Å) and Bond-Valence Sums ($\sum_s$) for $K_5In_3Si_7O_{21}$ (**1**) and $K_4In_2Si_8O_{21}$ (**2**)

compound **1**				compound **2**			
K(1)−O(20)	2.777(3)	K(1)−O(17)	2.998(3)	K(1)−O(10)	2.778(2)	K(1)−O(1)	3.018(2)
K(1)−O(4)	2.813(3)	K(1)−O(13)	3.280(3)	K(1)−O(4)	2.894(2)	K(1)−O(2)	3.150(2)
K(1)−O(8)	2.845(3)	K(1)−O(6)	3.324(3)	K(1)−O(5)	2.912(2)	K(1)−O(3)	3.242(2)
K(1)−O(15)	2.847(3)			K(1)−O(9)	2.926(2)	K(1)−O(7)	3.282(2)
$\sum_s$[K(1)−O] = 0.80				$\sum_s$[K(1)−O] = 0.79			
K(2)−O(18)	2.726(3)	K(2)−O(16)	2.963(3)	K(2)−O(1)	2.664(2)	K(2)−O(11)	2.813(2)
K(2)−O(6)	2.733(3)	K(2)−O(5)	3.094(3)	K(2)−O(9)	2.696(2)	K(2)−O(8)	2.831(2)
K(2)−O(1)	2.797(3)	K(2)−O(2)	3.221(3)	K(2)−O(11)	2.770(2)	K(2)−O(2)	2.842(2)
$\sum_s$[K(2)−O] = 0.80				$\sum_s$[K(2)−O] = 1.09			
K(3)−O(8)	2.762(3)	K(3)−O(7)	3.005(3)	In(1)−O(10)	2.041(2)	In(1)−O(5)	2.130(2)
K(3)−O(14)	2.771(3)	K(3)−O(3)	3.157(3)	In(1)−O(11)	2.085(2)	In(1)−O(9)	2.139(2)
K(3)−O(9)	2.890(3)	K(3)−O(4)	3.193(3)	In(1)−O(1)	2.096(2)		
K(3)−O(16)	2.960(3)			$\sum_s$[In(1)−O] = 2.95			
$\sum_s$[K(3)−O] = 0.81				Si(1)−O(1)	1.576(2)	Si(1)−O(3)	1.631(2)
K(4)−O(12)	2.749(3)	K(4)−O(9)	3.005(3)	Si(1)−O(2)	1.642(2)	Si(1)−O(4)	1.624(2)
K(4)−O(3)	2.784(3)	K(4)−O(19)	3.109(3)	$\sum_s$[Si(1)−O] = 4.07			
K(4)−O(2)	2.840(3)	K(4)−O(11)	3.248(3)	Si(2)−O(2)	1.628(2)	Si(2)−O(6)	1.5983(6)
K(4)−O(7)	2.884(3)			Si(2)−O(5)	1.575(2)	Si(2)−O(7)	1.620(2)
$\sum_s$[K(4)−O] = 0.85				$\sum_s$[Si(2)−O] = 4.21			
K(5)−O(21)	2.699(3)	K(5)−O(10)	2.928(3)	Si(3)−O(9)	1.584(2)	Si(3)−O(7)	1.626(2)
K(5)−O(20)	2.815(3)	K(5)−O(15)	2.957(3)	Si(3)−O(8)	1.615(2)	Si(3)−O(3)	1.641(2)
K(5)−O(17)	2.859(3)	K(5)−O(18)	3.051(3)	$\sum_s$[Si(3)−O] = 4.09			
K(5)−O(14)	2.924(3)			Si(4)−O(4)	1.651(2)	Si(4)−O(10)	1.588(2)
$\sum_s$[K(5)−O] = 0.94				Si(4)−O(8)	1.652(2)	Si(4)−O(11)	1.587(2)
In(1)−O(15)	2.060(3)	In(1)−O(9)	2.088(3)	$\sum_s$[Si(4)−O] = 4.06			
In(1)−O(18)	2.084(3)	In(1)−O(12)	2.088(3)				
In(1)−O(20)	2.083(3)						
$\sum_s$[In(1)−O] = 3.08							
In(2)−O(14)	2.070(3)	In(2)−O(3)	2.099(3)				
In(2)−O(1)	2.078(3)	In(2)−O(5)	2.185(2)				
In(2)−O(21)	2.256(3)	In(2)−O(11)	2.258(3)				
$\sum_s$[In(2)−O] = 3.07							
In(3)−O(8)	2.079(3)	In(3)−O(21)	2.165(3)				
In(3)−O(17)	2.095(3)	In(3)−O(11)	2.193(3)				
In(3)−O(6)	2.108(2)	In(3)−O(5)	2.334(2)				
$\sum_s$[In(3)−O] = 3.05							
Si(1)−O(1)	1.596(3)	Si(1)−O(3)	1.600(3)				
Si(1)−O(2)	1.647(3)	Si(1)−O(4)	1.656(3)				
$\sum_s$[Si(1)−O] = 4.00							
Si(2)−O(4)	1.657(3)	Si(2)−O(6)	1.594(3)				
Si(2)−O(5)	1.616(3)	Si(2)−O(7)	1.643(3)				
$\sum_s$[Si(2)−O] = 3.97							
Si(3)−O(7)	1.656(3)	Si(3)−O(9)	1.591(3)				
Si(3)−O(8)	1.594(3)	Si(3)−O(10)	1.634(3)				
$\sum_s$[Si(3)−O] = 4.07							
Si(4)−O(10)	1.644(3)	Si(4)−O(12)	1.604(3)				
Si(4)−O(11)	1.613(3)	Si(4)−O(13)	1.649(3)				
$\sum_s$[Si(4)−O] = 3.97							
Si(5)−O(13)	1.656(3)	Si(5)−O(15)	1.606(3)				
Si(5)−O(14)	1.594(3)	Si(5)−O(16)	1.634(3)				
$\sum_s$[Si(5)−O] = 4.02							
Si(6)−O(16)	1.647(3)	Si(6)−O(18)	1.605(3)				
Si(6)−O(17)	1.599(3)	Si(6)−O(19)	1.649(3)				
$\sum_s$[Si(6)−O] = 4.00							
Si(7)−O(19)	1.635(3)	Si(7)−O(21)	1.608(3)				
Si(7)−O(20)	1.585(3)	Si(7)−O(2)	1.637(3)				
$\sum_s$[Si(7)−O] = 4.09							

the potassium cations. The InO_6 octahedra are quite distorted as shown by the In−O distances ranging from 2.07 to 2.33 Å and the small O−In−O bond angles (72.7−79.2°) subtended by each other. The octahedral distortion can be estimated by using the equation $\Delta = (1/6)\sum[(R_i - R_{av})/R_{av}]^2$, where R_i is the individual bond length and R_{av} is the average bond length.[12] The calculation gives $\Delta = 6.4 \times 10^{-3}$ and $\Delta = 7.5 \times 10^{-3}$ for In(1)O_6 and In(2)O_6, respectively, which are a hundred times larger than that of a regular InO_6 octahedron as observed in $Rb_3In(H_2O)Si_5O_{13}$.[3d] The In⋯In distance within a dimer is 3.140(1) Å, which is comparable to that of In_2O_3 of the corundum structure (3.114(1) Å).[13] All indium atoms are trivalent as indicated by bond-valence sums, which are 3.08 for In(1), 3.07 for In(2), and 3.05 for In(3), respectively.[14] The potassium cations which are located in the cavities within the framework occupy five nonequivalent sites. On the basis of the maximum cation−anion distance by Donnay and Allmann,[15] a limit of 3.35 Å was set for K−O interactions; all potassium cations are 7-coordinate except K(2) which is 6-coordinate.

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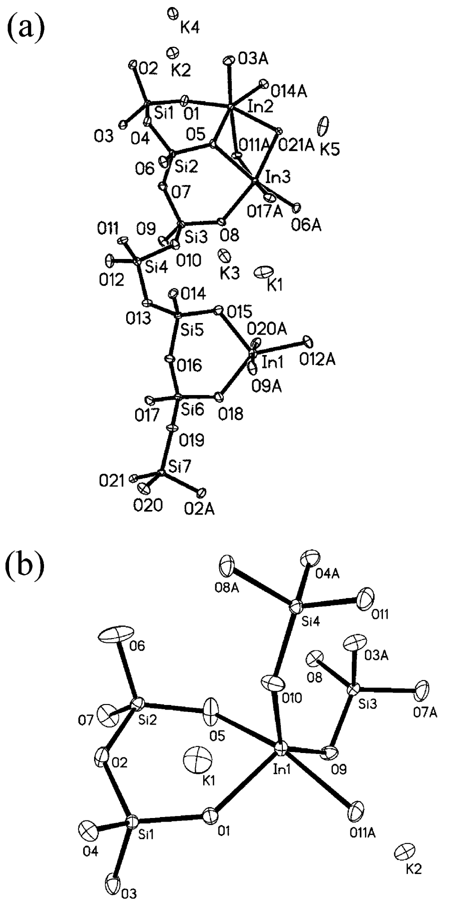

Figure 1. Structural building units of (a) $K_5In_3Si_7O_{21}$ (**1**) and (b) $K_4In_2Si_8O_{21}$ (**2**) showing atom labeling scheme. Thermal ellipsoids are shown at 50% probability.

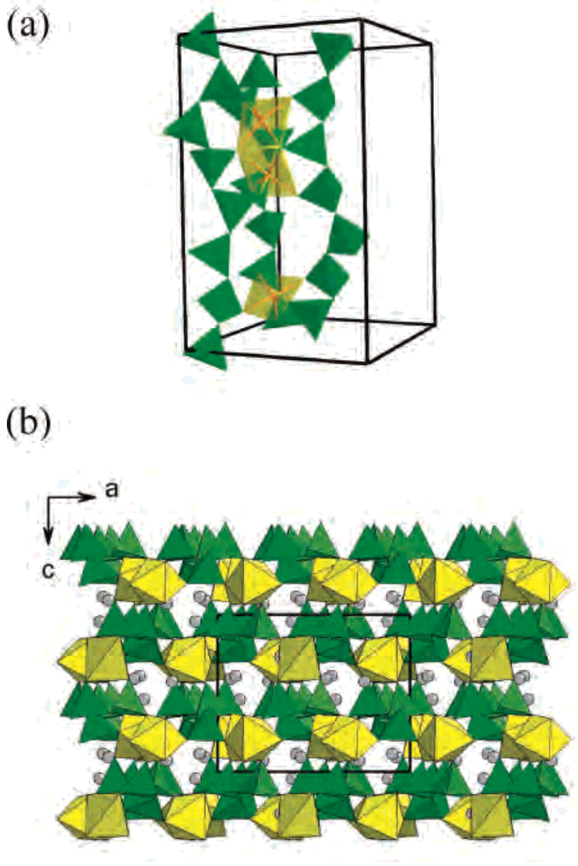

Figure 2. (a) Connectivity between silicate chains and In−O polyhedra within the unit cell of **1**. (b) Structure of **1** viewed along the *b* axis. The yellow polyhedra represent In_2O_9 face-sharing octahedral dimers and InO_5 trigonal bipyramids, and the green tetrahedra are SiO_4 tetrahedra. Gray circles are potassium atoms.

The bond-valence sums for the potassium cations range from 0.80 to 0.94.[14]

As shown in Figure 1b, the structure of **2** is constructed from the following structural elements: 2 potassium sites, 1 InO_5 distorted square pyramid, and 4 SiO_4 tetrahedra. Three of the silicate tetrahedra share corners with each other to form loop-branched dreier single chains with six-membered rings extending parallel to the *a* axis. Adjacent single chains are interconnected by Q^2 SiO_4 tetrahedra to form a 3D silicate framework containing channels delimited by 14-membered rings, which extend along the *a* axis (Figure 3a). The InO_5 distorted square pyramids are located within the 14-ring channels and share their oxygen atoms with the silicate framework to form channels in which the potassium cations reside (Figure 3b). The bond-valence sum for In(1) is 2.96, indicating that the indium atom is trivalent. The coordination numbers of the potassium cations are 8 for K(1) and 6 for K(2). The bond-valence sums for K(1) and K(2) are 0.79 and 1.09, respectively.

Most silicate frameworks have 4-connected SiO_4 tetrahedra which is defined as connectedness $s = 4$. For interrupted frameworks which contain more than one type of silicate tetrahedra, the mean value of $\langle s\rangle$ must be in the range of $2 < \langle s\rangle < 4$.[16] Compound **2** demonstrates a novel tectosilicate structure type of $\langle s\rangle < 3$, which is composed of secondary and tertiary SiO_4 tetrahedra with a ratio of 1:3. To our knowledge, only two tectosiliates have been reported for which $\langle s\rangle < 3$, namely, $LiNa_2K(Fe,Mg,Mn)_2Ti_2[Si_8O_{22}]O_2$ (neptunite)[17] and $Rb_3In(H_2O)Si_5O_{13}$.[3d] The former contains equal numbers of secondary and tertiary SiO_4 tetrahedra to form a structure resembling the $Zn(CN)_2$-topological type. The latter, which was reported by us, consists of $InO_5(H_2O)$ octahedra and a silicate framework belonging to the $CdSO_4$-topological type. Upon heating to 600 °C, $Rb_3In(H_2O)Si_5O_{13}$ loses the coodinated water molecule, while the crystal structure remains intact to give the anhydrous compound $Rb_3InSi_5O_{13}$ which contains InO_5 square pyramids.[18] If the dehydrated crystals are exposed to air at about 60% relative humidity for several hours, the water molecule can be restored up to 50% based on single-crystal structure refinements.

To our knowledge, the indium borate, $Li_3InB_2O_6$ is the only known compound which contains InO_5 trigonal bipyra-

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(18) Crystal data for $Rb_3InSi_5O_{13}$: colorless tabular crystal of dimensions 0.2 × 0.1 × 0.1 mm, $T = 100$ K, monoclinic, space group *Cc* (No. 9), $a = 8.876(1)$ Å, $b = 11.479(2)$ Å, $c = 13.967(2)$ Å, $\beta = 102.967(2)°$, $V = 1386.8(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 3.447$ g cm^{-3}, $\lambda = 0.71073$ Å, $\mu = 12.663$ mm^{-1}, 5025 reflections measured, 2239 unique reflections with $I > 2\sigma(I)$ ($2\theta_{max} = 56.6°$, $R_{int} = 0.0522$), GOF = 1.007, R1 = 0.0327, wR2 = 0.0689. The final cycles of least-squares refinement included atomic coordinates and anisotropic thermal parameters for all atoms.

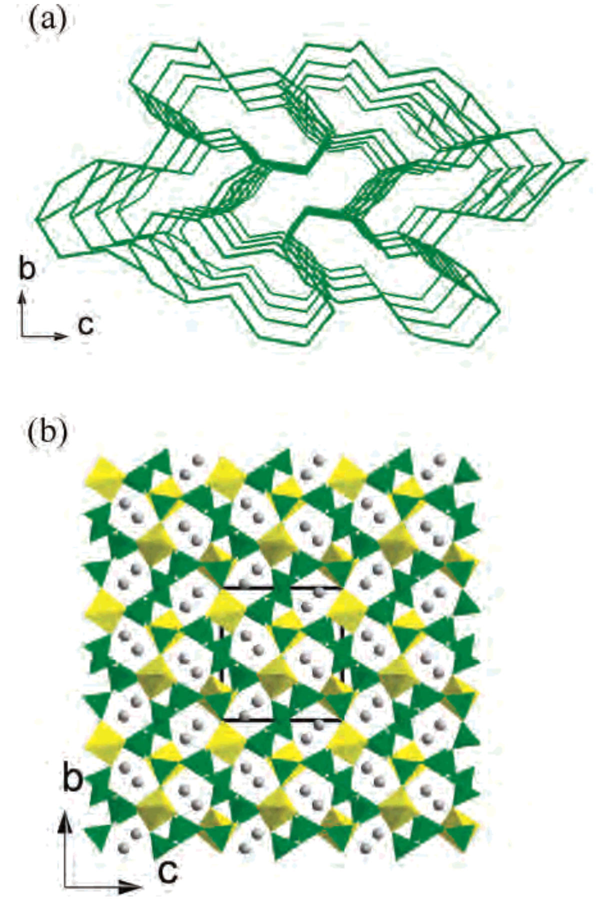

Figure 3. (a) Silicate framework of **2** viewed along the *a* axis. In this simplified schematic diagram, a tetrahedral Si atom is located at the intersection of the lines. A line is drawn between two Si atoms and the bridging oxygen atoms are not shown. (b) Structure of **2** viewed along the *a* axis. The yellow and green polyhedra are InO_5 square pyramids and SiO_4 tetrahedra, respectively. Gray circles are potassium atoms.

mids.[19] The structure consists of BO_3 triangles sharing corners with InO_5 to form a 3D framework. A 5-coordinate MO_5 polyhedron may exhibit three kinds of environments, square pyramid (SP), trigonal bipyramid (TB), and half SP-half TB.[20] The parameter τ defined by Addison et al.[21] as $\tau = (\beta - \alpha)/60$ was calculated (β and α are the largest O−In−O angles of the InO_5 polyhedron) to distinguish different environments. The value is equal to 0 for an ideal SP and to 1 for a TB. The τ value is 0.02 for $Rb_3InSi_5O_{13}$, 0.6 for **1**, 0.36 for **2,** and 0.76 for the indium borate mentioned above.

^{29}Si MAS NMR. The local environment of the SiO_4 unit is sensitively reflected in the chemical shift of the central Si atom. Figure 4 shows the one-pulse ^{29}Si MAS NMR spectrum of **1**. Four resonances at −77.9, −80.3, −81.9, and −84.2 ppm with an intensity ratio of 2:3:1:1 are observed. There are seven unique Si sites which can be classified into four groups, according to the coordination environment of SiO_4 as shown in Table 3. The resonance at −77.9 ppm is assigned to the group of Si(4) and Si(7), and the resonance at −80.3 ppm is assigned to the group of Si(3), Si(5), and Si(6), on the basis of the intensity ratio. Si(2) is connected to one more indium atom via the μ_3-O atom as compared to Si(1). In general, the substitution by Al of each of four silicons surrounding the central Si of a Q^4 unit in an aluminosilicate results in the ^{29}Si chemical shift of about 5 ppm toward less negative values. Therefore, Si(1) is assigned to the resonance at −84.2 ppm, and Si(2) is assigned to the next low-field peak at −81.9 ppm. The chemical shift of Si(1) is also comparable with that of a Q^4(2In) unit in $Na_5InSi_4O_{12}$.[3c]

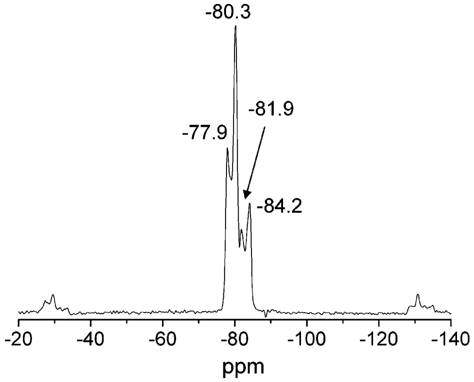

Figure 4. ^{29}Si one-pulse MAS NMR spectrum of **1** acquired at a spinning speed of 6 kHz. The isotropic peaks are labeled and other small peaks are spinning sidebands.

Table 3. Coordination Environment of Silicates in $K_5In_3Si_7O_{21}$ (**1**)

environment of SiO_4	atom
$2SiO_4$, InO_5, $2InO_6$ (via μ_3-O)	Si(4), Si(7)
$2SiO_4$, InO_5, InO_6	Si(3), Si(5), Si(6)
$2SiO_4$, InO_6, $2InO_6$ (via μ_3-O)	Si(2)
$2SiO_4$, $2InO_6$	Si(1)

In summary, two indium silicates containing varied In−O coordination geometries were synthesized by a flux-growth method. The two structures contain InO_5 polyhedra with different τ values related to different geometries as TB or SP. Compound **1** is unprecedented in that two different coordination geometries of indium, In_2O_9 and InO_5, coexist. The peaks in the ^{29}Si NMR spectrum can be assigned according to the intensity ratio and the occurrence of indium atoms in the second coordination sphere of the silicon. When the cooling procedure of the flux-growth experiment was changed, a second phase with a 3D framework structure containing only InO_5 square pyramids cocrystallized. They are the first examples of flux synthesis of indium silicates. Further research to incorporate transition metals or lanthanides into the indium silicate open frameworks by high-temperature high-pressure hydrothermal or flux growth methods is in progress.

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Supporting Information Available: Crystallographic data for **1** and **2** in CIF format and experimental and simulated X-ray powder patterns for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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