Synthesis of Nanoporous Cubic In(CN)$_3$ and In$_{1-x}$Ga$_x$(CN)$_3$ and Corresponding Inclusion Compounds

Darrick Williams, J. Kouvetakis,* and M. O'Keeffe

Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287

Anhydrous In(CN)$_3$ and In$_{1-x}$Ga$_x$(CN)$_3$ phases with empty Prussian-blue-type structures have been prepared via low-temperature solution methods utilizing molecular templating agents. Quantitative X-ray powder diffraction was used to refine the In(CN)$_3$ cubic structure in which In is octahedrally surrounded by an average of three C and three N atoms. The symmetry is $Pm\bar{3}m$, $a = 5.627(1)$ Å, and the In−(C,N) and C−N bond lengths are 2.251(1) and 1.125(1) Å, respectively. The compound reversibly incorporates krypton atoms into the empty cavities to form In(CN)$_3$·Kr, which is readily identified by powder diffraction. Similar inclusion systems with *n*-hexane in the porous framework are also synthesized. In$_{1-x}$Ga$_x$(CN)$_3$ solid solutions are formed by suitable combinations of the binary systems and have lattice constants adjustable between 5.293 Å for Ga(CN)$_3$ and 5.627(1) Å for In(CN)$_3$. The variation of the lattice parameters with composition obeys Vegard's Law.

Introduction

We recently reported several related routes to the synthesis of Ga(CN)$_3$ with a cubic Prussian blue structure.[1] The most convenient is the reaction of GaCl$_3$ with SiMe$_3$CN to produce solid Ga(CN)$_3$ with elimination of volatile SiMe$_3$Cl. Attempts to produce In(CN)$_3$ with a cubic Prussian blue structure analogous to that of Ga(CN)$_3$ under the same reaction conditions were unsuccessful or at best produced mixtures of very poorly crystalline materials. Earlier reports of a monoclinic form of In(CN)$_3$[2] with a unit cell similar to that of InBr$_3$[3] seemed plausible because the molar volumes of the alkali cyanides and bromides are known to be very similar. This material was obtained at very low yields as a high-temperature phase in the course of an attempt to prepare indium oxycyanide, InOCN. However, we have now found that a modification of our synthetic procedure (essentially involving a low-temperature solution method) produces well-formed crystalline In(CN)$_3$ with the cubic structure in nearly quantitative yield. A key feature of the new synthesis is the use of solvents (*n*-hexane and diethyl ether) that may act as templating molecules and which can subsequently be removed with retention of the crystalline network. The material has a larger lattice parameter than other known Prussian blue compounds and the volume per formula unit (179 Å^3) is significantly greater than that of Ga(CN)$_3$ (149 Å^3), and much larger than the earlier-reported form of In(CN)$_3$ (126 Å^3). As we describe below, the material readily incorporates noble gases such as Kr and solvent molecules such as *n*-hexane in the empty cavities, and like Ga(CN)$_3$ it should readily lead to derivative framework structures and interpenetrating lattices.[1] Also of interest is the synthesis of a continuous solid solution In$_{1-x}$Ga$_x$(CN)$_3$ in which the lattice parameter (*a*) varies linearly with composition (*x*).

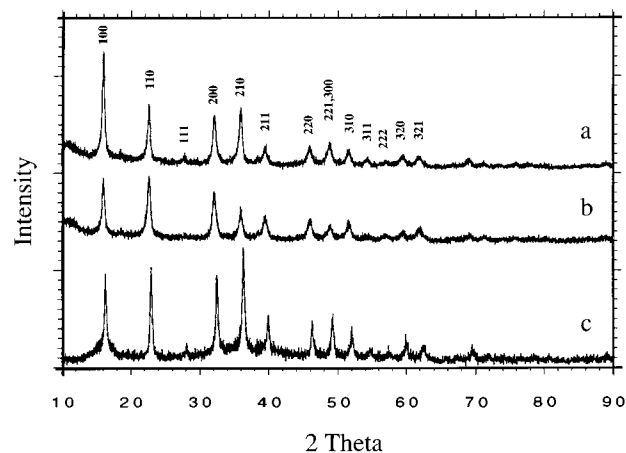**Figure 1.** X-ray diffraction pattern of the simple cubic structure for (a) pure In(CN)$_3$, (b) In(CN)$_3$·Kr, and (c) In(CN)$_3$·hexane. Note the decrease in intensity of the 100 reflection in (b) and (c) relative to (a), which is consistent with the incorporation of guest species in the cavities. Also note the absence of the 111 reflection and the relative increase of the 200 relative to the 210 in the In(CN)$_3$·Kr pattern. These diffraction features are virtually identical with calculated patterns.

Results and Discussion

In(CN)$_3$ was prepared by treatment of freshly sublimed InCl$_3$ with an excess of SiMe$_3$CN in dry ether−hexane solutions. The SiMe$_3$Cl byproduct and the unreacted SiMe$_3$CN were removed by filtration to give a colorless solid that was purified by extraction with warm hexane. The infrared (IR) spectrum of the material has weak absorptions similar to the vibrational modes of hexane as well as absorptions characteristic of the In(CN)$_3$ framework (see below). The X-ray diffraction pattern indicates a simple cubic structure as shown in Figure 1c. All peaks could be indexed using a primitive cubic cell with $a \approx$ 5.65 Å, and no systematic absences were found. The only structure likely for cubic In(CN)$_3$ with a small primitive cell is a disordered one with In at the cell corners octahedrally coordinated by CN ligands and joined by C−N bonds aligned

(1) Brousseau, L. C.; Williams, D. J.; Kouvetakis J.; O'Keeffe M. *J. Am. Chem. Soc.* **1997**, *119*, 6292.

(2) Goglin, P. L.; McColm, I. J.; Shore, R. J. *J. Chem. Soc. A* **1966**, 1314. The lattice parameters for In(CN)$_3$ in the abstract are clearly incorrect; we have used the parameters reported in the text.

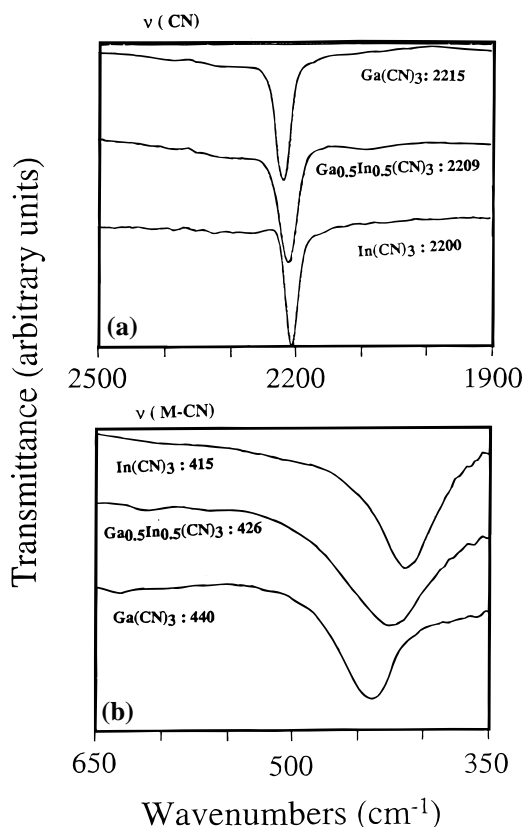(3) Staffel, T.; Meyer, C. *Z. Anorg. Allg. Chem.* **1988**, *563*, 27.

Figure 2. Infrared spectra of $Ga(CN)_3$, $In_{0.5}Ga_{0.5}(CN)_3$, and $In(CN)_3$ showing (a) the peaks corresponding to the C−N stretching frequency and (b) the peaks corresponding to the M−(C,N) stretching bands.

Figure 3. Unit cell of $In(CN)_3$ constructed by use of van der Waals radii of the In and (C, N). The large spheres at the corners of the cell represent the In atoms. The interstitial site at the center of the cell is occupied by Kr atoms in $In(CN)_3 \cdot Kr$.

along the cell edges, as in $Ga(CN)_3$.[1,4] Surprisingly the intensity of the 100 reflection is substantially lower than calculated for an empty Prussian blue structure relative to the intensities of the 110 and 200 reflections. These differences in relative intensities between experimental and calculated patterns are consistent with the presence of a scattering center such as hexane inside the cavity. Heating at 180 °C under dynamic vacuum resulted in removal of the guest species and the final product gave the predicted diffraction pattern for the empty Prussian blue structure for pure $In(CN)_3$ as shown in Figure 1a (note the differences in relative X-ray peak intensities between $In(CN)_3 \cdot$ hexane and pure $In(CN)_3$ in Figure 1c and a, respectively). For this material $a = 5.627(1)$ Å, and from a refinement of the data using a disordered model similar to that[4] for $Ga(CN)_3$, the C−N bond length was found to be 1.125(1) Å, a value normal for metal cyanides. The In−(C,N) bond distance is 2.251(1) Å, slightly longer than the Ga−(C,N) distance in $Ga(CN)_3$. The material is moisture sensitive but is remarkably stable in dry oxygen. It decomposes to indium metal and $(CN)_2$ under dynamic vacuum at 400 °C but when heated in nitrogen remains stable up to 500 °C. In the presence of ammonia at 400 °C the colorless $In(CN)_3$ decomposes to a black solid that was shown by X-ray diffraction to contain poorly crystalline InN.

The IR spectrum of the empty $In(CN)_3$ structure shows only two absorptions at 2200 cm^{-1} [$\nu(CN)$] and 415 cm^{-1} [$\nu(M-CN)$] (Figure 2). These values are comparable with those of the isostructural $Ga(CN)_3$ analogue which has IR absorbances at 2215 and 440 cm^{-1}. Vibrational modes corresponding to CH groups are absent indicating the complete elimination of
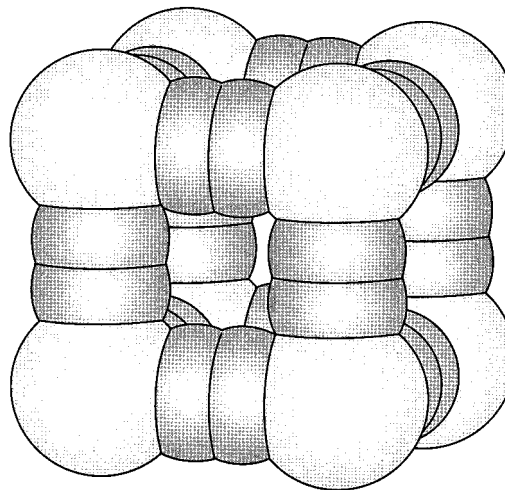
the hexane and/or ether from the pores of the material. Mass spectra obtained by the direct vaporization of the compound at 350 °C reveal the molecular ion $In(CN)_3$ at m/z 192.

An investigation was made into the possibility of inclusion of noble-gas guest species into the $In(CN)_3$ empty framework. Incorporation of Kr atoms in the three-dimensional pore structure was readily achieved at room temperature with high-pressure Kr gas. The $In(CN)_3$ sample was first degassed at 120 °C under dynamic vacuum in a stainless steel vessel and immediately thereafter high-purity Kr was condensed at −196 °C. The mixture was kept under pressure for several days before it was separated and the relative amounts of the components were measured. The weight of the $In(CN)_3$ material is increased by an amount that indicates an approximate composition In-$(CN)_3 \cdot Kr$. The presence of Kr atoms in the pores of the framework structure was best demonstrated by X-ray diffraction. The diffraction pattern of $In(CN)_3 \cdot Kr$ (Figure 1b) reveals a marked decrease in intensity of the 100 and the 210 reflections relative to the intensity in the 110 and 200 reflections in comparison with pure $In(CN)_3$ (Figure 1a). This indicates the presence of a considerable electron density (such as Kr) at the center of the cell. A comparison between the calculated and experimental diffraction patterns of $In(CN)_3 \cdot Kr$ showed good agreement and further supports Kr incorporation. Evacuation of $In(CN)_3 \cdot Kr$ at room-temperature resulted in loss of some Kr which was collected in a cold trap (−196 °C) and identified by mass spectrometry. However, desorption of the remainder of the Kr atoms from the $In(CN)_3$ lattice required prolonged pumping at elevated temperatures. Reinsertion of the Kr in the host lattice occurs readily by use of the protocol described above indicating that the process is indeed reversible unlike the inclusion of *n*-hexane molecules in $In(CN)_3$ which is not reversible. The experimental diffraction patterns of $In(CN)_3$ before and after intercalation illustrate that the integrity of the host lattice is preserved after deintercalation.

Attempts to incorporate Xe into $In(CN)_3$ did not succeed even at high temperatures and pressures. In addition, we did not observe any incorporation of Kr into the smaller pores of the analogous $Ga(CN)_3$. These results suggest that the cavity size is critical. Figure 3 shows a unit cell of the $In(CN)_3$ structure with the atoms represented by spheres of radius equal to their van der Waals radii i.e., 1.6 Å for C,N (these are disordered in

(4) Williams, D. J.; Partin, D. E.; Lincoln, F. J.; Kouvetakis, J.; O'Keeffe, M. *J. Solid State Chem.* **1997**, *134*, 164−169.
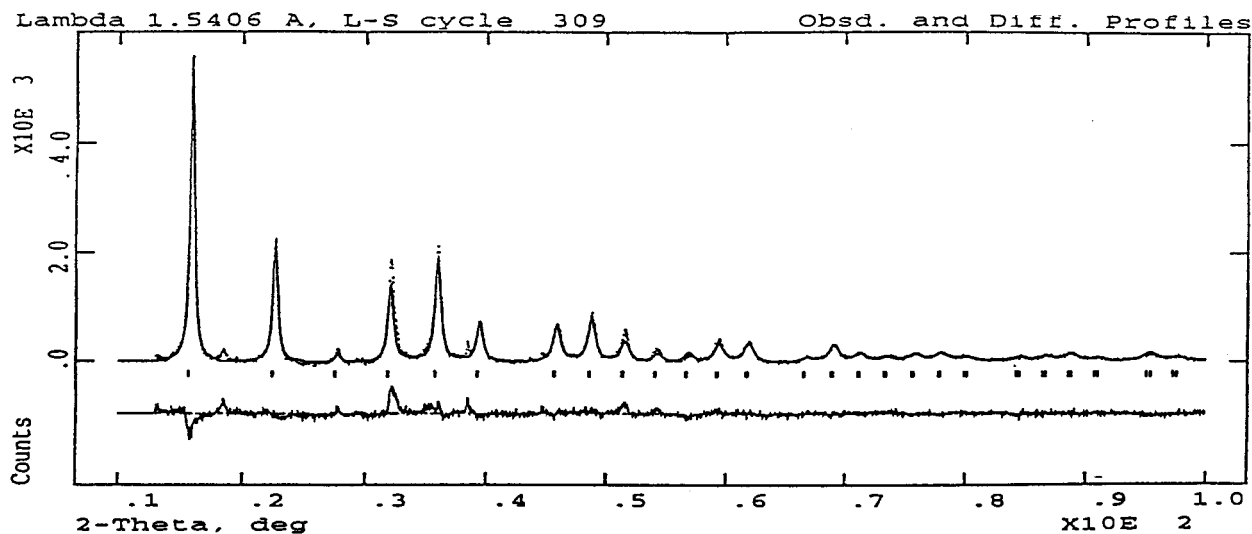
Figure 4. X-ray powder diffraction profile fit for In(CN)₃. Top: fit to the experimental data. Bottom: difference (experimental − calculated) on the same scale.

the structure) and 1.9 Å for In.[5] The cavity in the center of the cube at $^1/_2$, $^1/_2$, $^1/_2$ can accommodate a sphere of radius 2.9 Å. The aperture in the face of the cube has a radius of only 1.2 Å if rigid C−N units are considered to block the way, but the face diagonal distance between In atoms could allow an atom of a radius of 2.0 Å to enter if the CN groups do not act as a rigid obstruction (notice that the C, N atoms typically have large atomic displacement parameters in cyanides of this type[4]). It is of interest therefore that Kr, which has a radius of 2.02 Å, can be readily absorbed in and desorbed from the cavity, but no incorporation of Xe, which has a radius of 2.16 Å, has been observed.

Cyanides of the Prussian blue type have long been known to possess zeolitic properties although in early work the extent to which the observed phenomena were due to surface adsorption was not clear.[6] A resurgence of interest[7,8] in adsorption and catalysis by Prussian blue cyanides has focused on materials that are thought to have large cavities formed by the absence of metal atoms from the ideal framework displayed in Figure 3. These are generally materials with ideal composition $M_x[M(CN)_6]$ with $x < 1$ (for the ideal framework $x = 1$) and with indeterminate amounts of water or related ligands in the cavities. We believe that Ga(CN)₃ and In(CN)₃ are the first to be prepared anhydrously, and because of their simple composition the structures can readily be studied by quantitative X-ray diffraction.

Also of interest is the preparation of ternary compounds and solid solutions $[Ga_{1−x}In_x(CN)_3]$ in the Ga−In−CN system because it allows us to vary unit cell parameter and hence pore size. Unit cell parameters ranging from 5.293 Å for Ga(CN)₃ to 5.627 Å for In(CN)₃ are possible. The synthetic approach involved reactions of the desired metal halide mixture with a large excess of SiMe₃CN in an ether−hexane solution. The resulting colorless precipitates were isolated and annealed in nitrogen at 200−250 °C for several days and then examined by IR spectroscopy and X-ray diffraction. Several samples with

varying Ga/In ratio were prepared and characterized. The IR spectra of all samples exhibited only the expected absorptions for ν(C−N) and ν(M−CN), and their frequency values were intermediate to those of the pure binary systems. For example, ν(C−N) for Ga₀.₅In₀.₅(CN)₃ is at 2208 cm⁻¹, which is intermediate to that for Ga(CN)₃ and In(CN)₃ (2215 and 2200 cm⁻¹ respectively; Figure 2A). Similarly ν(M−CN) for Ga₀.₅In₀.₅-(CN)₃ is at 426 cm⁻¹, which is intermediate to those for Ga(CN)₃ and In(CN)₃ (440 and 415 cm⁻¹, respectively, Figure 2B). The diffraction patterns of all samples were consistent with disordered primitive cubic structures as expected for random solid solutions (no ordered phase formation was observed) and have unit cell parameters intermediate to those of the pure binary components (see below). In general, the lattice parameter of an intermediate phase may be obtained by linear interpolation between those of the binary components in accordance with Vegard's law.

Experimental Section

General Procedures. Reactions were performed under prepurified nitrogen with standard Schlenk and drybox techniques. Solvents were dried and distilled prior to use. The FTIR spectra were recorded from Nujol and fluorolube mulls or in a 10-cm gas cell with KBr windows on a Nicolet Magna-IR spectrometer. Electron impact mass spectra were collected on a Finnigan-MAT model 312 mass spectrometer (IE = 70 eV, source T = 225 °C). Indium trichloride (99.99% purity, Cerac), gallium trichloride, and trimethylsilyl cyanide (Aldrich) were used as received.

Synthesis of In(CN)₃. To a suspension of InCl₃ (1.15 g, 5.2 mmol) in diethyl ether (30 mL), was added dropwise a solution of (CH₃)₃-SiCN (1.70 g, 17.2 mmol) in hexane (20 mL) at 0 °C. The mixture was stirred at room temperature for 12 h during which time it gradually darkened to a light brown color. The precipitate was isolated by filtration and was pumped at 40 °C under vacuum for several hours to remove any remaining (CH₃)₃SiCl and excess (CH₃)₃SiCN. The colorless product was heated in hexane for 12 h, and subsequently it was extracted several times with warm hexane to remove the soluble impurities. The IR spectrum showed that the material was a cyanide and the powder X-ray pattern revealed a simple cubic structure indicative of an inclusion Prussian blue compound. Heating at 160−200 °C under vacuum for 12 h removed the remaining volatile components to yield a solid in nearly quantitative yield which has an X-ray pattern characteristic of an empty Prussian blue structure.

Synthesis of In₁₋ₓGaₓ(CN)₃. In a similar manner, a suspension of GaCl₃ (0.7879 g, 3.56 mmol) and InCl₃ (0.6272 g, 3.56 mmol) in 30

(5) Bondi, A. *J. Phys. Chem.* **1994**, *68*, 441.

(6) Seifer, G. B. *Russ. J. Inorg. Chem.* **1962**, *7*, 899 and references therein.

(7) (a) Cartraud, P.; Cointot, A.; Renaud, A. *J. Chem. Soc., Faraday Trans.* **1981**, *77*, 1561. (b) Boxhoorn, G.; Moolhuysen, J.; Coolegam, J. G.; van Santen, R. A. *J. Chem. Soc., Chem. Commun.* **1985**, 1305. (c) Kuyper, J.; Boxhoorn, G. *J. Catalysis* **1987**, *105*, 163.

(8) Taylor, R. J.; Drago, R. S.; Hage, J. P. *Inorg. Chem.* **1992**, *31*, 253.

mL ether was treated dropwise with a solution of $SiMe_3CN$ (2.1204 g, 21 mmol) in hexane (20 mL). The solution was stirred for 12 h after which time the colorless precipitate was isolated by filtration, heated in dry hexane for several hours, and then washed with hexane several times to yield $In_{0.5}Ga_{0.5}(CN)_3$ quantitatively. Other compositions in the In−Ga−C−N system were prepared by virtually the same procedure. The products were characterized by IR to show that each material is a cyanide, and by powder X-ray diffraction to obtain the lattice parameter of the cubic cell. The unit cell parameter for $Ga_{0.5}In_{0.5}(CN)_3$ [5.464(3) Å] is nearly the average of those for $Ga(CN)_3$ [5.295(2) Å][1,4] and $In(CN)_3$ [5.627(1) Å]. Other compositions prepared and the corresponding lattice constants are $In_{0.75}Ga_{0.25}(CN)_3$, $a = 5.537(2)$ Å; and $In_{0.25}Ga_{0.75}(CN)_3$, $a = 5.428(2)$ Å.

Structure of $In(CN)_3$. Samples for X-ray powder diffraction were loaded into an environmental cell with a Kapton window and data were collected with a Rigaku D/max IIB diffractometer using Cu Kα radiation. The data refined consisted of one set, collected with a step size 0.01° (90 s per degree) and collection time 2 h for $2\theta = 5-90°$. The refinement using the general structure analysis system, *GSAS*,[9] a Rietveld refinement code, fitted 11 600 data points. For the final refinement $\chi^2 = 6.13$, $R_p = 8.9\%$, $R_{wp} = 11.5\%$ for a total of 15 parameters. The only structural parameters are the lattice parameter and the (C,N) positional parameter. The (C,N) atoms are at x, 0, 0

(9) Larson, A. C.; Von Dreele, R. B. *GSAS: Generalized Structure Analysis System*; LANSCE, MS-H805; Manual Lujan Neutron Scattering Center, Los Alamos, NM, 1989.

and the refined value is $x = 0.4000(1)$. Observed and calculated histograms are compared in Figure 4. The main differences, which appear as characteristic "anthill" shapes are due to difficulties in fitting the peak shapes (rather than integrated intensities).

Conclusion

We have prepared the previously unknown cubic form of $In(CN)_3$ and we have shown that it contains an open framework structure which has previously been observed for $Ga(CN)_3$. Our synthetic method is based on complete displacement of the chloride ligands from $InCl_3$ by CN in the presence of simple organic molecular templates. The low-temperature synthetic approach and the incorporation of templating molecules probably play a key role in the formation of this new structure. We have also shown that $In(CN)_3$ can combine with $Ga(CN)_3$ to form solid solutions in which the lattice parameter varies smoothly with concentration across the entire compositional range.

IC971638N