Indium(III) Amides and Nitrides

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Indium amide ($In(NH_2)_3$) was synthesized from a reaction between InI_3 and 3 equiv of KNH_2 in anhydrous liquid ammonia at 25 °C. The white solid is nearly insoluble in ammonia but dissolves in NH_3 solutions of KNH_2 to form potassium indium amides, $K_xIn(NH_2)_{3+x}$. Sodium indium amides can be obtained similarly. A reaction between InI_3, 3 equiv of LiI, and 6 equiv of KNH_2 affords $Li_3In(NH_2)_6$, which is insoluble in ammonia. Indium nitride is obtained from the thermolysis of $In(NH_2)_3$, $Na_xIn(NH_2)_{3+x}$, and $K_xIn(NH_2)_{3+x}$. Reduction to indium metal also occurs during thermal decomposition of some of the potassium indium amides. Thermolysis of $Li_3In(NH_2)_6$ affords the new ternary nitride Li_3InN_2, an orange, water-sensitive electrical insulator, whose powder pattern was indexed to a cubic primitive cell of $a = 10.136(8)$ Å. Direct reaction between Li_3N and InN produces InLi in addition to Li_3InN_2, and thus is not a viable synthesis route to this new nitride.

There has been some recent interest in the synthesis of new ternary nitrides and new synthetic methods for known binary nitrides.[1] The group 13 nitrides are technologically important, BN[2] and AlN being refractory and electrically insulating, while GaN and InN[4] are semiconductors.[3] Thin films of alloys such as AlN–GaN and GaN–InN have been deposited by various methods,[3,5] and ternary compounds with lithium nitride are known for BN, AlN, and GaN.[6] Indium nitride has been less well studied than the others, probably a result of its low thermal stability.[7] Some ternary nitrides of indium with Ca, Sr, and Ti are known,[8] but a lithium indium nitride has not been reported. Thermal decomposition of metal amides [$M(NH_2)_n$] has proven to be a fruitful synthetic method for a number of thermally unstable binary nitrides,[9] and this method has not been applied to the synthesis of indium nitrides. This work is a study of the synthesis of indium(III) amides, $In(NH_2)_3$ and $M_xIn(NH_2)_{3+x}$ (M = alkali metal), the thermolysis of those amides, and the direct combination of Li_3N and InN.

Experimental Section

General Comments. All manipulations were performed under helium atmosphere in a Vacuum/Atmospheres Dri-Lab, under vacuum, or in anhydrous ammonia. The thick-walled Pyrex H-tube (apparatus A) for work with liquid ammonia at room temperature is illustrated in Figure 1, and the apparatus (B) used at −33 °C consists of an ordinary H-tube with a vacuum-jacketed frit section. *In all operations with liquid ammonia at room temperature in apparatus A, the tip O-rings were omitted from the Kontes valves, and such operations were conducted behind a safety shield, with heavy leather gloves, heavy jacket, and a face shield used during handling.* Sonication was done in a 8845-3 Cole-Parmer ultrasonic cleaner, with the hood sash one-third open to ensure a good cooling air flow. *Apparatus A will burst if allowed to overheat in the sonicator when containing liquid ammonia.* Lithium nitride was purchased from Alfa Products Inc., and anhydrous ammonia was obtained from Air Products Inc. The ammonia was very dry as received and was only dried over sodium when small quantities of reactants were used. Potassium amide was made from a reaction between anhydrous ammonia and potassium metal at room temperature in a 150-mL high-pressure stainless steel tube equipped with a suitable Hoke valve. For example, 75 mL of NH_3 and 6 g of K were allowed to react for 4 days, and 7.62 g of the white solid was isolated after NH_3 removal. Indium(III) iodide was made by a literature procedure.[10] Powder X-ray diffraction data were collected on a Phillips diffractometer with a graphite crystal monochromator and using Cu radiation. Infrared spectra were obtained as KBr pellets or gas samples on a Perkin-Elmer 1430 ratio-recording spectrometer at room temperature. Elemental analyses were performed by E+R Microanalytical Laboratory Inc., Corona, NY.

Synthesis of $In(NH_2)_3$. Potassium amide (0.34 g, 6.2 mmol) was loaded into the reaction flask of apparatus B, and InI_3 (1.00 g, 2.0 mmol) was loaded into the filter arm. Liquid ammonia (30 mL) was condensed onto the KNH_2 and allowed to warm to −33 °C (1 atm), at which point the InI_3 was added. After 0.5 h of stirring, the white precipitate was filtered off, washed by recondensing the ammonia into the reaction flask and filtering four times, and dried under vacuum, affording 0.23 g (70%) of the off-white solid. Anal. Found (calcd) for InN_3H_6: C, 0.21 (0); H, 3.99 (3.71); In, 70.46 (70.49); N, 25.81 (25.80). A cleaner (totally iodide-free and white) product with sharper powder diffraction lines was prepared at room temperature with several hours of sonication. For example, 0.268 g (81% yield) of $In(NH_2)_3$ was obtained from 1.02 g of InI_3 and 0.36 g of KNH_2. XRD [d, Å (I/I_0)]: 5.628 (53)*, 5.144 (4), 4.932 (22), 4.695 (9), 4.413 (15), 3.817 (2), 3.283 (10), 3.055 (3), 2.993 (49), 2.835 (11)*, 2.648 (100), 2.565 (6), 2.526 (2), 2.482 (5), 2.216 (6), 2.200 (5), 2.141 (3), 2.062 (97), 2.058 (44)*, 1.952 (10), 1.914 (8), 1.893 (5)*, 1.857 (1), 1.785 (7), 1.734 (33), 1.702 (4), 1.658 (48), 1.601 (37)*, 1.530 (3), 1.501 (17), 1.481 (13), 1.453 (19), 1.423 (8)*, 1.367 (2), 1.349 (2), 1.328 (26), 1.284 (17), 1.279 (7), 1.243 (1), 1.177 (13), 1.150 (2), 1.136 (15), 1.114 (24), 1.101 (7), 1.073 (2), 1.065 (4), 1.055 (20), 1.034 (4), 1.014 (2), 1.002 (6), 0.987 (9), 0.975 (13).

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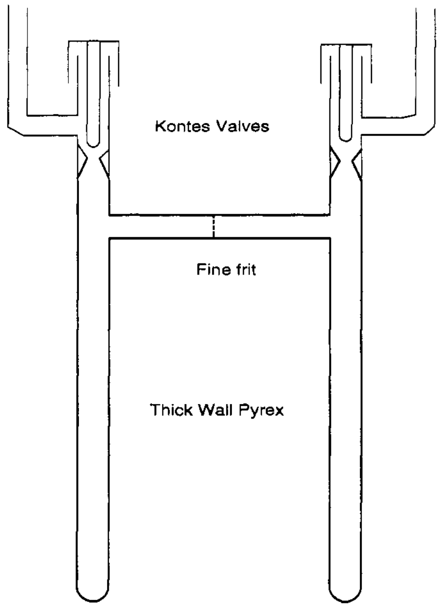

Figure 1. Apparatus for reactions in liquid ammonia at room temperature.

Crystals of $In(NH_2)_3$ were obtained by adding a NH_3 solution of $K_3In(NH_2)_6$ to a cleaned piece of porous Vycor glass[11] in apparatus A. The mixture was allowed to stand for 1 day as $In(NH_2)_3$ slowly crystallized on the tube and the Vycor glass. The crystals were identified as $In(NH_2)_3$ by IR spectroscopy. The material in solution was determined to be $K_2In(NH_2)_5$ by powder diffraction. An attempt to fully solve the crystal structure of $In(NH_2)_3$ was unsuccessful, possibly due to twinning. The crystals are hexagonal (a = 6.021(1) Å, c = 17.032(5) Å), with extinction $l = 3n$. The only prominent peaks in the powder pattern of a crushed crystal are indicated with an asterisk above. Apparently the precipitated product contains multiple phases.

Synthesis of $K_xIn(NH_2)_{3+x}$. $x = 2$. Indium amide (0.074 g, 0.45 mmol) and KNH_2 (.050 g, 0.90 mmol) were mixed in apparatus A with 10 mL of dried NH_3, and the mixture was stirred to completely dissolve the starting materials. After filtration, the ammonia was evaporated and the white solid $K_2In(NH_2)_5$ was dried under vacuum and scraped out of the tube; 60 mg (48%) was isolated. Anal. Found (calcd) for $K_2InN_5H_{10}$: C, <0.1 (0); H, 3.77 (3.69); In, 41.81 (42.04); N, 25.56 (25.64); K, 28.88 (28.63). XRD [d, Å (I/I_0)]: 5.594 (40), 3.167 (31), 3.074 (36), 2.810 (27), 2.682 (67), 2.416 (3), 2.131 (30), 1.881 (100), 1.619 (33), 1.564 (19), 1.539 (12), 1.412 (8), 1.296 (7), 1.193 (6), 1.089 (5), 1.067 (5), 1.029 (5). An attempt at preparing the $x = 1$ compound involved the combination of 1.23 mmol of $In(NH_2)_3$ and 1.23 mmol of KNH_2 in 10 mL of dried NH_3 and 16 h of stirring at 20 °C, and in a similar manner 233 mg of white solid was isolated. A 101-mg portion was set aside in a tube under vacuum for 107 days at room temperature. From the latter, 3.6 mg of NH_3 and 91.5 mg of black residue were isolated.

$x = 3$. A solution of KNH_2 (0.667 g, 12.1 mmol) was added to a solution of InI_3 (1.00 g, 2.02 mmol) in apparatus A. The mixture was sonicated for 1 h, and the precipitate was filtered off and washed three times; 0.3223 g (48%) was isolated. Anal. Found (calcd) for $K_3InN_6H_{12}$: C, 0 (0); H, 3.43 (3.69); N, 25.73 (25.60); K, 35.91 (35.73); In, 35.47 (34.98). The compound was also made similarly to $K_2In(NH_2)_5$. XRD [d, Å (I/I_0)]: 6.360 (2), 5.552 (14), 5.375 (10), 4.847 (3), 3.217 (23), 3.084 (26), 2.815 (5), 2.700 (100), 2.494 (2), 2.124 (6), 1.951 (25), 1.889 (21), 1.670 (8), 1.632 (11), 1.570 (5), 1.551 (12), 1.418 (4), 1.358 (4), 1.281 (4), 1.256 (3), 1.230 (10), 1.200 (5), 1.141 (3), 1.105 (3), 1.047 (2), 1.035 (2).

$x = 4$. Attempts to prepare this compound were made in a manner similar to that for $K_2In(NH_2)_5$. All products were characterized by powder diffraction and IR spectroscopy.

Synthesis of Li–In–N Materials. (a) Precursor Method. InI_3 (0.50 g, 0.10 mmol) and an appropriate amount of LiI (depending on desired Li:In ratio) were put in one leg of H-tube A, and a stoichiometric amount of KNH_2 was put in the other side. Several milliliters of NH_3 was added to each side, the KNH_2 solution was added to the iodides at room temperature, and its side of the H-tube was washed once to transfer all the KNH_2. The mixture was sonicated for 3–5 h and then filtered; and the product was washed by condensing the NH_3 onto it four times. The white lithium indium amide(s) were then dried under dynamic vacuum. Anal. Found (calcd) for $Li_3In(NH_2)_6$: Li, 9.22 (8.98); In, 49.26 (49.54); N, 36.03 (36.26); H, 4.99 (5.21). A sample was also prepared at −33 °C using a 3:1 Li:In ratio, but elemental analysis of the amide product yielded a 2.8 Li:In ratio. Found: Li, 8.35; In, 49.11; N, 31.31; H, 4.40.

Amides were heated in a Pyrex vessel under dynamic vacuum to ~370 °C, the vessel was backfilled with N_2, and the amides were then pyrolyzed to 420–435 °C for 2–16 h; for example, 183.4 mg (98.8% yield) of Li_3InN_2 was obtained from 263 mg of $Li_3In(NH_2)_6$. Anal. Found (calcd) for Li_3InN_2: Li, 12.74 (12.72); In, 70.29 (70.16); N, 17.20 (17.12); H, 0 (0); C, 0 (0).

(b) Solid State Reaction Method. Li_3N (0.135 g) and InN (0.50 g) were ground with an agate mortar and pestle and pressed into a pellet at 50 000 psi, and the pellet was put in a Pyrex tube under an N_2 atmosphere. The sample was heated under dinitrogen as described previously and the resulting material characterized by powder diffraction.

Powder pattern of $Li_3In(NH_2)_6$ [d, Å (I/I_0)]: 7.464 (11), 6.355 (5), 5.757 (7), 5.147 (14), 4.976 (26), 4.911 (22), 4.741 (9), 4.590 (10), 4.112 (10), 3.800 (7), 3.700 (2), 3.450 (100), 3.355 (5), 3.121 (6), 2.912 (72), 2.818 (11), 2.699 (12), 2.570 (2), 2.548 (2), 2.517 (4), 2.443 (3), 2.391 (9), 2.251 (20), 2.156 (5), 2.107 (10), 1.948 (4), 1.917 (6), 1.868 (19), 1.847 (4), 1.798 (69), 1.786 (38), 1.757 (2), 1.683 (6), 1.644 (4), 1.621 (4), 1.592 (25), 1.540 (4), 1.528 (6), 1.466 (4), 1.419 (32), 1.403 (9), 1.379 (6), 1.362 (3), 1.314 (4), 1.303 (8), 1.294 (10), 1.281 (7), 1.266 (8), 1.191 (3), 1.145 (2), 1.134 (2), 1.113 (7), 1.087 (2), 1.054 (12), 1.044 (6), 1.037 (20), 0.992 (6).

Synthesis of InN. (a) Pyrolysis of $In(NH_2)_3$. $In(NH_2)_3$ (141 mg, 0.87 mmol) was heated under vacuum to 207 °C, evolving ammonia (see Figure 2). The product was then heated to 415 °C under N_2 (1 atm) to afford brownish-black InN (0.110 g, 99% yield). The powder pattern has sharp lines.

(b) Pyrolysis of $Na_xIn(NH_2)_{3+x}$. $NaNH_2$ (0.50 g, 12.8 mmol) was added to an ammonia solution of InI_3 (1.02 g, 2.05 mmol) at −33 °C, and the mixture was stirred for 1 h. The mixture was filtered, and the precipitate was washed three times with recondensed ammonia. After ammonia removal, the precipitate (0.304 g) was dried under vacuum. A portion of the precipitate (0.153 g) was heated to 360 °C under static N_2 for 1 h. Wet ethanol was added to residue, and when reaction subsided, solids were washed with water and more ethanol and dried under vacuum at 170 °C for 12 h. Isolated yield: 0.027 g (20% based on InI_3); some product undoubtedly held up on frit. Anal. Found (calcd) for InN: In, 89.27 (89.13); N, 10.67 (10.87); I, 0 (0). The powder pattern shows a very well crystallized InN.

Sodium indium amides (x = 1–3) were also prepared from direct reaction between $In(NH_2)_3$ and $NaNH_2$ in liquid ammonia, similar to the preparation of $K_2In(NH_2)_5$, and thermolyzed as described below.

Thermolysis of Amides. All data in Figure 2 were obtained by heating the amide in a Pyrex vessel on a vacuum line under dynamic vacuum, with identical valve openings in every case. The total pressures were obtained before the trap with a thermocouple gauge, and noncondensable (at −196 °C) pressures were obtained after the trap with a penning gauge. Figure 2 displays total integrated quantities calculated from the progressive sum of $(P_n + P_{n-1})(T_n - T_{n-1})/2$ at each data point, after the data were normalized to 1 mol. The number of molar equivalents of NH_3 emitted to a particular temperature was also determined by trapping and measurement on the vacuum line.

Results and Discussion

Synthesis of Amides. Indium amide and lithium indium amide are readily prepared by metathetical reactions in liquid ammonia at room temperature (eqs 1 and 2). The nearly insoluble products

$$InI_3 + 3KNH_2 \rightarrow In(NH_2)_3 + 3KI \qquad (1)$$

$$InI_3 + 3LiI + 6KNH_2 \rightarrow Li_3In(NH_2)_6 + 6KI \qquad (2)$$

precipitate from solution, and sonication is used to ensure complete reaction. A very slight excess of KNH_2 is necessary in each case to prevent iodide contamination of the product. Performance of these reactions at −33 °C usually results in impure products. Attempts to prepare $Li_xIn(NH_2)_{3+x}$ with $x < 3$ afford mixtures

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[11] Corning Glass Corp.; 40-Å pore size. Cleaned by boiling in H_2O_2 and H_2O for several hours each and heating under dynamic vacuum to 400 °C.

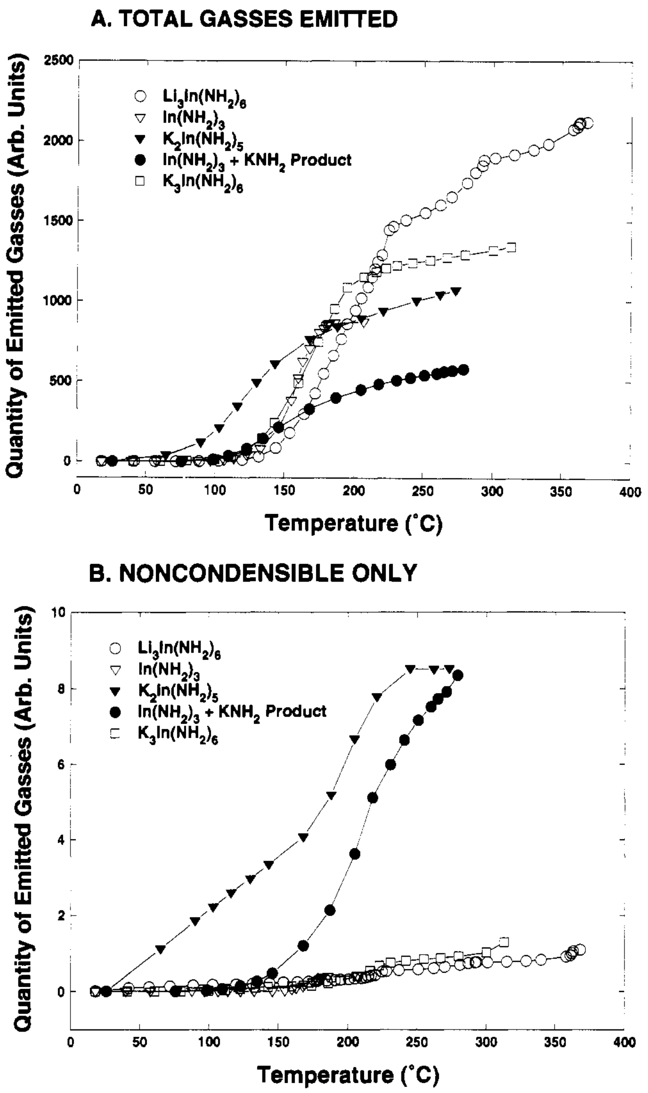

Figure 2. Decomposition profiles of indium amides.

of $In(NH_2)_3$ and $Li_3In(NH_2)_6$, as determined by the presence of the 3364-cm^{-1} peak in the IR spectrum and by the presence of peaks for both compounds in the powder diffraction pattern. When the Li:In ratio is greater than 3, mixtures of $Li_3In(NH_2)_6$ and $LiNH_2$ result. Notice that two of the IR absorptions of $Li_3In(NH_2)_6$ are at the same frequency as the absorptions of $LiNH_2$. When excess $LiNH_2$ is present the 3311- and 3254-cm^{-1} peaks increase in intensity relative to the other peaks, but the relative intensity never drops below the values in Table 1, even in samples prepared with a Li:In ratio of 2. These results indicate that $Li_3In(NH_2)_6$ might actually be an adduct or cocrystallized product of $LiNH_2$ and another lithium indium amide such as $Li_2In(NH_2)_5$ or $LiIn(NH_2)_4$. For comparison, the only lithium aluminum amide to be reported is $LiAl(NH_2)_4$.[12]

Potassium indium amides are prepared from reactions between InI_3 and KNH_2 or by dissolving $In(NH_2)_3$ in an ammonia solution of KNH_2. When the latter are combined in a 1:1 mole ratio, the $In(NH_2)_3$ dissolves, possibly forming $KIn(NH_2)_4$ in solution, but the white product remaining after evaporation of the NH_3 solvent has the infrared spectra and powder patterns of both $K_2In(NH_2)_5$ and $In(NH_2)_3$. This white solid rapidly evolves ammonia to afford a dark red product that turns black after several weeks. In one experiment, 0.5 equiv of NH_3 was evolved over 107 days at room temperature. The infrared spectrum of the latter decomposition product showed only the peaks for $K_2In(NH_2)_5$; the peaks for $In(NH_2)_3$ disappeared.

A 2:1 KNH_2:$In(NH_2)_3$ ratio yields the highly soluble $K_2In(NH_2)_5$, which is stable at room temperature for several months, and combination in a 3:1 ratio affords the extremely air-sensitive $K_3In(NH_2)_6$, which precipitates from solution. A material of formula $K_4InN_5H_8$ was reported to be formed from a reaction between $InBr_3$ and KNH_2.[13] However, combination of KNH_2 and $In(NH_2)_3$ in a 4:1 mole ratio affords a product containing $K_3In(NH_2)_6$ and excess KNH_2, according to the IR spectrum and the powder pattern. With the analogous aluminum and gallium systems, only the $MM'(NH_2)_4$ and $M_2M'(NH_2)_5$ (M = Li, Na, K; M' = Al, Ga) compounds have been reported.[14] In all cases, the NH_2 stretching frequencies are in the same range (3400–3200 cm^{-1}) reported for alkali metal amidoaluminates and amidogallates (Table 1).

Thermolysis of Amides to Nitrides. Thermolysis experiments were conducted in a vacuum system on many of the indium amides, including both single compounds and mixtures. A plot of the quantity of evolved gasses vs temperature (Figure 2) gives a semiquantitative picture of the stabilities of the various amides. Amorphous materials were obtained from the thermolysis of $In(NH_2)_3$, $K_xIn(NH_2)_{3+x}$, and $Na_xIn(NH_2)_{3+x}$ up to 300 °C; with $In(NH_2)_3$, 1.8 equiv of NH_3 is evolved up to this temperature. Crystalline InN products were only obtained by heating under 1 atm of dinitrogen from 300 to approximately 400 °C. (Indium nitride is unstable under vacuum above 300 °C; a dinitrogen atmosphere is necessary to prevent decomposition.[7]) One might expect the intermediate stages between $In(NH_2)_3$ and InN to contain imide (NH^{2-}) species, but this could not be confirmed by infrared spectroscopy. Indium nitride has a broad, (>1500-cm^{-1} width) intense intrinsic absorption centered between 2800 and 3300 cm^{-1}.[4d] The thermolysis products of $In(NH_2)_3$ show similar broad, intense absorptions that undoubtedly mask any N–H stretching bands that may be present. The centers of the IR absorptions of the latter products appear at 2000, 2350, 2850, and 3000 cm^{-1} for samples prepared at 210, 300, 400, and 415 °C, respectively.

Indium amide decomposes cleanly and quantitatively to InN (eq 3), and $K_2In(NH_2)_5$ affords InN along with liberated KNH_2.

$$In(NH_2)_3 \rightarrow InN + 2NH_3 \qquad (3)$$

$$K_2In(NH_2)_5 \rightarrow InN + 2KNH_2 + 2NH_3 \qquad (4)$$

$$Na_xIn(NH_2)_{3+x} \rightarrow InN + xNaNH_2 + 2NH_3 \qquad (5)$$

The black product from $KNH_2 + In(NH_2)_3$ behaves differently, producing on thermolysis In metal in addition to InN. Substantial amounts of noncondensable gases are also evolved during the thermolysis of $In(NH_2)_3 + KNH_2$ and $K_2In(NH_2)_5$ (Figure 2B). Some In metal is also formed from the decomposition of $K_3In(NH_2)_6$, which produces poorly crystalline InN and 2 equiv of NH_3. A possible explanation for In metal production is reduction by potassium amide or potassium metal (a small amount of K sublimes during the thermolyses). However, neither indium metal nor appreciable noncondensable gases are produced from the thermal decomposition of $Na_xIn(NH_2)_{3+x}$ (x = 1–3). The presence of excess sodium amide results in an InN product with sharp diffraction lines; $NaNH_2$ apparently acts as a flux to afford well-crystallized InN, but the higher melting KNH_2 does not.

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Table 1. N–H Vibrational Frequencies (cm^{-1}) of Various Compounds (KBr Pellet)

	NH_2[a] (rel intens)			
compd	str	bend	compd	N–H[c]
$LiNH_2$	3311 (60), 3255 (100)	1540, 1565	Li_3InN_2[b]	3180 vw
KNH_2	3253 (90), 3205 (100)	1552	$Li_{2.9}InN_2H_x$	3180 w
$In(NH_2)_3$	3364 (60), 3285 (100)	1553	$Li_3InN_2{\cdot}0.5Li_2NH$	3165 m
$Li_3In(NH_2)_6$	3346 (65), 3328 (45), 3311 (80), 3285 (35), 3254 (100)	1547	$Li_3InN_2{\cdot}Li_2NH$	3155 s
			Li_2NH	3150 s
$K_2In(NH_2)_5$	3346 (20), 3271 (100), 3221 (95)	1587, 1561, 1534		
$K_3In(NH_2)_6$	3272 (100), 3221 (100)	1560		
$LiAl(NH_2)_4$	3407, 3397, 3357[d]		BeNH	3330[e]
	3335, 3296		CaNH	3183[e]
$KAl(NH_2)_4$	3420, 3384, 3353, 3319[d]		SrNH	3143[e]
$NaAl(NH_2)_4$	3386, 3374, 3324, 3310[d]		BaNH	3056[e]
$Na_2Ga(NH_2)_5$	3360, 3340, 3290, 3280, 3260, 3210	1580, 1545[f]		

[a] All compounds produce sharp lines for N–H stretch and broad lines for N–H bend. [b] Residual N–H. [c] Bending vibrations not observed for lithium imides. [d] Reference 12 (Nujol). [e] Reference 14d. [f] Reference 14a (Nujol).

Table 2. Powder Diffraction Pattern for Li_3InN_2

$1/d^2$				$1/d^2$			
calc	obs	I/I_0	*h k l*	calc	obs	I/I_0	*h k l*
0.03002	0.03029	14	1 1 1	0.55723	0.55600	2	5 4 4, 7 2 2
0.05954	0.05904	9	2 1 1	0.57671	0.57566	6	5 5 3, 7 3 1
0.08898	0.08927	14	2 2 1, 3 0 0	0.60589	0.60467	3	7 3 2, 6 5 1
0.10857	0.10878	21	3 1 1	0.62536	0.62580	22	8 0 0
0.11839	0.11881	9	2 2 2	0.65454	0.65416	2	7 3 3
0.13793	0.13763	12	3 2 1	0.68373	0.68256	1	6 5 3
0.15749	0.15787	75	4 0 0	0.71291	0.71226	1	8 3 0, 6 6 1
0.16726	0.16758	11	4 1 0, 3 2 2	0.76152	0.76117	1	7 5 2
0.18681	0.18710	15	3 3 1	0.78098	0.78176	32	8 4 0
0.21611	0.21629	4	3 3 2	0.81013	0.81152	5	9 1 1, 7 5 3
0.26492	0.26499	10	5 1 1, 3 3 3	0.83931	0.83860	2	7 6 1, 9 2 1 6 5 5
0.29418	0.29460	5	5 2 1	0.86846	0.86856	3	9 2 2, 8 5 0 8 4 3, 7 6 2
0.31369	0.31364	100	4 4 0	0.88790	0.88832	2	9 3 1
0.34294	0.34259	11	5 3 1	0.91705	0.91784	1	9 3 2, 7 6 3
0.37218	0.37262	5	5 3 2, 6 1 1	0.93648	0.93767	44	8 4 4
0.40142	0.40103	5	5 4 0, 4 4 3 6 2 1	0.96563	0.96552	3	9 3 3, 7 7 1 7 5 5
0.42091	0.42199	4	5 3 3	0.99478	0.99442	1	10 1 1, 7 7 2
0.43065	0.43090	4	6 2 2	1.02392	1.02444	1	10 2 1, 8 5 4
0.45013	0.45001	2	6 3 1	1.04334	1.04315	3	9 5 1, 7 7 3
0.46961	0.46990	27	4 4 4				
0.47935	0.48012	6	7 0 0, 6 3 2				
0.49882	0.49783	6	5 5 1, 7 1 1				
0.52803	0.52900	3	7 2 1, 6 3 3 5 5 2				

The thermolysis of $Li_3In(NH_2)_6$ to ~370 °C under vacuum and then to 420–430 °C under N_2 affords the orange compound Li_3InN_2 in nearly quantitative yield (eq 6). Both the initial heating

$$Li_3In(NH_2)_6 \rightarrow Li_3InN_2 + 4NH_3 \qquad (6)$$

under vacuum, which results in loss of 3.7 equiv of NH_3, and the final heating under dinitrogen are necessary. Conducting the entire thermolysis under vacuum results in a red compound with strong N–H bands in the IR spectrum (3135, 3110 cm^{-1}) which are in the correct region for imide (NH^{2-}) species.[14d] Heating $Li_3In(NH_2)_6$ under a static N_2 atmosphere results in side reactions between the evolved NH_3 and the product, producing a mixture containing InN, $LiNH_2$, and In metal. No attempts were made to conduct any thermolyses under flowing dinitrogen. Thermal decompositions of mixtures of $Li_3In(NH_2)_6$ and $LiNH_2$ (from InI_3 + >3LiI + $x$$KNH_2$) result in orange solid solutions of Li_3InN_2 and Li_2NH. The IR spectrum of the latter indicates that these are not simple mixtures, since the N–H stretching frequency increases smoothly as the proportion of Li_3InN_2 in the mixture increases (see Table 1). X-ray powder diffraction experiments show Li_3InN_2 to have a primitive cubic cell of a = 10.136(8) Å (Table 2). Since these cell dimensions are almost exactly twice those of Li_2NH[15] (5.05 Å), it is considered likely that solid solutions form with Li_2NH. The powder patterns of these solid solutions are nearly identical to the Li_3InN_2 pattern. When lithium-deficient starting materials are thermolyzed (mixtures of $Li_3In(NH_2)_6$ and $In(NH_2)_3$), a red product is formed, which becomes darker as the lithium deficiency increases. When the lithium deficiency is substantial, In metal is also formed during the thermolysis. The powder diffraction pattern of this red product is very similar to that of Li_3InN_2 but shows poor crystallinity. Many of the reflections with both odd and even indices are either missing or substantially reduced in intensity. Elemental analysis shows an N:In ratio of 2 in the lithium-deficient material, but hydrogen is also present, as charge balance would require for In(III) (empirical formulas: $Li_{2.8}InN_2H_{0.5}$, $Li_{2.9}InN_2H_{0.4}$). Lithium indium nitride is fairly stable under dinitrogen at temperatures of 520 °C for short periods of time (20 min), sustaining only surface decomposition, but when heated to 600 °C in a quartz vessel, it is rapidly decomposed to the Zintl phase Li_3In_2.[16]

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(16) Stohr, J.; Schaefer, Z. *Z. Naturforsch.* **1979**, *34B*, 653; JCPDS card 33-616.

Decomposition to a different Li–In Zintl phase, InLi,[17] occurred on heating to 450 °C for 16 h. Conductivity measurements show Li_3InN_2 to be an electrical insulator, with resistivity greater than 10^9 Ω cm.

Direct reaction between two nitrides is a standard method of ternary nitride synthesis and has been used to prepare Li_3AlN_2 and Li_3GaN_2.[6b] Thus the preparation of Li_3InN_2 was attempted in a similar manner:

process (15–16 h)	result/products	wt loss
$Li_3N + InN \xrightarrow{250\,°C}$	little reaction	1.4%
above product $\xrightarrow{350\,°C}$	Li_3InN_2, InLi, N_2, leftover Li_3N gray-black powder	5.9%
$Li_3N + InN \xrightarrow{435\,°C}$	$InLi + {}^2/_3Li_3N + {}^2/_3N_2$	11.5% (theory: 11.4%)

As shown above, Li_3InN_2 is formed around 350 °C, but the decomposition product InLi is already present is appreciable amounts. Higher temperatures result in complete decomposition of Li_3InN_2, with the amount of weight loss corresponding to a complete conversion to InLi. Either Li_3InN_2 is stabilized by the presence of Li_2NH and destabilized by Li_3N or the presence of InLi accelerates its decomposition. Direct reaction between these two nitrides does not appear to be a viable means of synthesis for Li_3InN_2.

Conclusions

The less soluble indium(III) amides, such as $In(NH_2)_3$ and $Li_3In(NH_2)_6$, are readily obtained by reactions between the metal iodides and KNH_2 in anhydrous ammonia at 25 °C, with sonication to ensure complete reaction. The more soluble derivatives, such as $K_2In(NH_2)_5$, can be prepared from the component amides in liquid ammonia. Thermal decompositions of $In(NH_2)_3$ and sodium indium amides afford InN quantitatively and may prove to be useful for the synthesis of this material, whereas potassium indium amides often undergo side reactions during thermal decomposition that produce indium metal. A new ternary nitride, Li_3InN_2, is obtained from the thermolysis of $Li_3In(NH_2)_6$. The absence of a direct reaction between Li_3N and InN to afford pure Li_3InN_2 illustrates the value of the amide precursor method for the synthesis of metastable ternary nitrides that are unobtainable by other means.

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