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# Synthesis of $Cl_2InN_3$, $Br_2InN_3$, and Related Adducts

**Cory Steffek, Jeff McMurran, Brett Pleune, and J. Kouvetakis***

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

**Thomas E. Concolino and Arnold L. Rheingold**

Department of Chemistry, University of Delaware,
Newark, Delaware 19716

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## Introduction

Recently we have reported several related routes for GaN synthesis utilizing inorganic azide precursors that incorporate hydride and halide ligands instead of organic groups. Our method for growth of epitaxial nitride films has been primarily focused on the thermodynamically driven decomposition of the newly synthesized $Cl_2GaN_3$, $H_2GaN_3$, $HBrGaN_3$, and $HClGaN_3$ azidogallanes on SiC and sapphire substrates.[1−3] Our search for analogous inorganic azides of indium that might be useful as precursors to InN has led to the development of the new and completely inorganic $X_2InN_3$ polymeric compounds (X = Cl, Br) and their molecular adducts with common Lewis bases such as tetrahydrofuran (THF) and pyridine. Related organometallic azides of indium, such as $N_3In[(CH_2)_3NMe_2]_2$ and the tris(pyridine) complex of $In(N_3)_3$, have been recently synthesized and were successfully used to prepare InN thin films and bulk powders.[4,5] In this note we describe the synthesis and properties of $Cl_2InN_3$ and $Br_2InN_3$ and present the solid-state molecular structure of a novel dinuclear $Cl_2InN_3(THF)_2$ complex which incorporates an $In_2N_2$ cyclic core formed by bridging azide ligands.

## Results and Discussion

$X_2InN_3$ (X = Cl, Br) are prepared by reaction of $SiMe_3N_3$ with $InX_3$ (X = Cl, Br) as air-sensitive, colorless solids which are nonexplosive and insoluble in organic solvents. Elemental analysis for C, H, N suggests the $X_2InN_3$ molecular formula for both compounds. The FTIR spectrum of $Cl_2InN_3$ is very simple and indicates a polymeric structure similar to that of $Cl_2GaN_3$. The spectrum is consistent with the absence of organic groups and shows the strong asymmetric stretch ($\nu_{as}$) of the azide ligand at 2132 $cm^{-1}$ as the strongest absorption band. Other notable features include $\nu_{sym}(N_3)$ at 1248 $cm^{-1}$, $\nu(In{-}N)$ at 390 $cm^{-1}$, $\delta(N_3)$ at 690 $cm^{-1}$, and $\gamma(N_3)$ at 575 $cm^{-1}$. The IR spectrum of $Br_2InN_3$ is similar to that of $Cl_2InN_3$ and includes vibrations at 2121 $cm^{-1}$ ($\nu_{asym}(N_3)$), 1257 $cm^{-1}$ ($\nu_{sym}$ $(N_3)$), 678 $cm^{-1}$ ($\delta(N_3)$), and 581 $cm^{-1}$ ($\gamma(N_3)$).

**Table 1.** Crystallographic Data for $[Cl_2InN_3(THF)_2]_2$

| | |
|---|---|
| formula | $C_{16}H_{32}Cl_4In_2N_6O_4$ |
| fw | 743.92 |
| space group | *Cmca* |
| *a*, Å | 12.337(2) |
| *b*, Å | 14.531(5) |
| *c*, Å | 15.649(2) |
| *V*, Å$^3$ | 2805.5(11) |
| *Z* | 4 |
| cryst color, habit | yellow block |
| *D*(calcd), g cm$^{-3}$ | 1.761 |
| $\mu$(Mo Kα), cm$^{-1}$ | 20.56 |
| temp, K | 254(2) |
| *T*(max)/*T*(min) | 0.7479/0.5774 |
| diffractometer | Siemens P4 |
| radiation | Mo Kα ($\lambda$ = 0.710 73 Å) |
| *R*(*F*), %$^a$ | 5.10 |
| $R_w(F^2)$, %$^a$ | 12.44 |

$^a$ Quantity minimized = $R_w(F^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$.

Pure $Cl_2InN_3$ does not have any appreciable vapor pressure, even at 150 °C, indicating that the compound is polymeric. The $Cl_2InN_3$ units are likely to form a chain in which the In atoms are linked by either the α- or the $\gamma$-nitrogen of the azide group. It has been previously established that in the polymeric $N_3In[(CH_2)_3NMe_2]_2$ compound cross-linking of the In atoms occurs via the $\gamma$-nitrogen of the $N_3$ ligand.[4] On the other hand, the $I_2GaN_3$ compound forms a similar polymeric structure in which cross-linking of the Ga atoms occurs via the α-nitrogen of the $N_3$ ligand.[6] The volatility of $Cl_2InN_3$ is significantly increased by coordinating the unsaturated unit with pyridine ligands to form the bis(pyridine) adduct $Cl_2InN_3(C_5H_5N)_2$. This compound is isolated as colorless crystals that sublime at 130 °C, $10^{-3}$ Torr. The $^1H$ and $^{13}C$ NMR spectra revealed the presence of the coordinated pyridine molecules, and the IR spectrum showed that the asymmetric stretch (2080 $cm^{-1}$) for the azide has shifted to a lower frequency with respect to that of pure $Cl_2InN_3$ (2132 $cm^{-1}$), which is consistent with the formation of the adduct. Electron impact mass spectrometric analysis by direct vaporization of the compound into the spectrometer revealed $[Cl_2InN_3]^+$ as the highest energy mass peak at 229 amu and other prominent peaks at 165, 150, and 80 amu corresponding to $[ClInN]^+$, $[ClIn]^+$, and $[C_5H_5N]^+$, respectively. The results of the elemental analysis for C, H, and N for the purified material are consistent with the $Cl_2InN_3(C_5H_5N)_2$ empirical formula.

$Cl_2InN_3$ also combines readily with THF to form the bis(THF) complex as colorless crystals. The structure of the adduct has been established by X-ray diffraction. The crystallographic data and interatomic distances and angles are summarized in Tables 1 and 2, respectively. An ORTEP diagram showing the molecular conformation and the atom-numbering scheme is presented in Figure 1.

The solid-state structure reveals dimeric units containing an In−N−In linkage rather than the In−N−N−N−In linkage which has been observed in the coordination polymer $(CF_3SO_3)In[(CH_2)_3NMe_2]_2(\mu\text{-}N_3)In[CH_2)_3NMe_2)]_2$.[4] As shown in Figure 1, the geometry of each In atom approximates a distorted octahedron with the Cl atoms and the $N_3$ groups residing in equatorial positions and the oxygen atoms of each THF molecule

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**Table 2.** Bond Lengths (Å) and Angles (deg) for $[Cl_2InN_3(THF)_2]_2$[a]

| | | | |
|---|---|---|---|
| In(1)−N(1)#1 | 2.242(8) | In(1)−N(1) | 2.242(8) |
| In(1)−O(2) | 2.257(10) | In(1)−O(1) | 2.293(13) |
| In(1)−Cl(1) | 2.385(3) | In(1)−Cl(1)#2 | 2.385(3) |
| O(1)−C(1) | 1.36(2) | O(1)−C(1)#2 | 1.36(2) |
| O(2)−C(3) | 1.418(12) | O(2)−C(3)#2 | 1.418(12) |
| N(1)−N(2) | 1.212(19) | N(1)−In(1)#1 | 2.242(8) |
| N(2)−N(3) | 1.128(18) | C(1)−C(2) | 1.39(3) |
| C(2)−C(2)#2 | 1.55(10) | C(3)−C(4) | 1.468(16) |
| C(4)−C(4)#2 | 1.33(2) | | |

| | | | |
|---|---|---|---|
| N(1)#1−In(1)−N(1) | 69.7(6) | N(1)#1−In(1)−O(2) | 88.2(2) |
| N(1)−In(1)−O(2) | 88.2(2) | N(1)#1−In(1)−O(1) | 88.6(3) |
| N(1)−In(1)−O(1) | 88.6(3) | O(2)−In(1)−O(1) | 176.1(4) |
| N(1)#1−In(1)−Cl(1) | 163.1(3) | N(1)−In(1)−Cl(1) | 93.4(3) |
| O(2)−In(1)−Cl(1) | 91.70(18) | O(1)−In(1)−Cl(1) | 90.7(2) |
| N(1)#1−In(1)−Cl(1)#2 | 93.4(3) | N(1)−In(1)−Cl(1)#2 | 163.1(3) |
| O(2)−In(1)−Cl(1)#2 | 91.70(18) | O(1)−In(1)−Cl(1)#2 | 90.7(2) |
| Cl(1)−In(1)−Cl(1)#2 | 103.53(17) | C(1)−O(1)−C(1)#2 | 109(3) |
| C(1)−O(1)−In(1) | 123.0(13) | C(1)#2−O(1)−In(1) | 123.0(13) |
| C(3)−O(2)−C(3)#2 | 108.2(12) | C(3)−O(2)−In(1) | 124.2(6) |
| C(3)#2−O(2)−In(1) | 124.2(6) | N(2)−N(1)−In(1)#1 | 124.9(3) |
| N(2)−N(1)−In(1) | 124.9(3) | In(1)#1−N(1)−In(1) | 110.3(6) |
| N(3)−N(2)−N(1) | 180.0(4) | C(2)−C(1)−O(1) | 112(3) |
| C(1)−C(2)−C(2)#2 | 104(3) | O(2)−C(3)−C(4) | 106.4(10) |
| C(4)#2−C(4)−C(3) | 109.2(7) | | |

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x, -y, -z + 1$; (#2) $-x, y, z$.

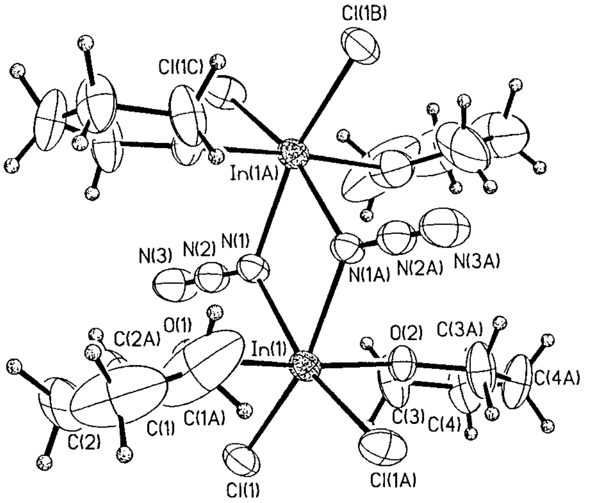

**Figure 1.** Molecular structure of $[Cl_2InN_3(THF)_2]_2$ displaying the planar $In_2N_2$ ring structure.

occupying the axial positions. Although there have been many hexacoordinate indium molecular compounds reported,[7] the $In_2N_2$ tetragonal framework has not been previously established in structures of group 13 inorganic and organometallic azides. Nevertheless, such a planar four-membered structure has been proposed for the dimeric azide of indium $[(C_2H_5)_2InN_3]_2$,[8] and similar $In_2N_2$ rings have been found in structures of organometallic amides of indium.[9,10] Other proven examples of molecular heterocyclics formed by means of bridged azides is the tetrameric gallane $(HClGaN_3)_4$,[1] with a cyclooctane-like structure, and the trimeric borane $(Cl_2BN_3)_3$,[11] with a cyclohexane-like conformation.

The bond angles In(1)−N(1)−In(1A) (110.3(6)°) and In(1)−N(1)−N(2) (124.9(3)°) as well as N(1A)−In(1)−Cl(1A) (93.4(3)°), N(1)−In(1)−Cl(1) (93.4(3)°), Cl(1A)−In(1)−Cl(1) (103.53(17)°), and N(1)−In(1)−N(1A) (69.7(6)°), clearly demonstrate that the entire $In_2N_2Cl_4$ molecular core of the $Cl_2InN_3(THF)_2$ dimer is planar. The deviation from the least-squares plane through the $In_2N_2$ central framework, including the azide branches and the Cl atoms, appears to be negligible (<0.01 Å). In addition, the bond angle O(1)−In(1)−O(2) at 176.1(4)° deviates slightly from the linear value and the N(1)−In(1)−O(1) and Cl(1)−In(1)−O(1) angles are 88.6(2) and 90.7(2)°, respectively. These values indicate that the dative In−O bonds are nearly orthogonal to the plane of the $In_2N_2Cl_4$ core.

The bonding parameters for the azide ligands are typical of those reported for other crystalline group 13 covalent azides. The N−N−N bond angle is exactly 180.0(4)°, and there are two distinct N−N distances within the azide group, with the shorter one corresponding to the terminal N−N bond (1.128(18) Å). The average bond distances for In−Cl (2.385(3) Å) and In−O (2.257(10) Å) are similar to those found for $InCl_3(THF)_3$ compound (2.420(4) and 2.235(10) Å, respectively).[6] The In−N bond distances (2.242(8) Å) are close to those found in the related organometallic azide $In(N_3)_3(C_5H_5N)_3$ (2.233(2) Å).[4]

The $X_2InN_3$ compounds reported in this note are stable and safe and potentially could be utilized to synthesize mixed hydride, $[HIn(X)N_3]$, and alkyl derivatives, $[HIn(CH_3)N_3]$, which should serve as precursors to InN materials. The report of a stable $InH_3$ complex, $InH_3[P(C_6H_{11})_3]$, suggests that a sterically stabilized $HIn(X)N_3$ compound may be possible.

**Safety Note.** We have not encountered any difficulties so far in handling the compounds described in this paper. However, azides are potentially explosive and should be handled with caution.

## Experimental Section

**General Considerations.** Reactions were performed under prepurified nitrogen using standard Schlenk and drybox techniques. Dry, air-free solvents were distilled from sodium benzophenone ketyl prior to use. $^1H$ NMR (300 MHz) and $^{13}C$ NMR (125.7 MHz) spectra were recorded on a Varian Gemini 300 and a Varian Unity 500 spectrometer, respectively. FTIR spectra were recorded on a Nicolet Magna-IR 550 spectrometer either as a Nujol mull between KBr plates or in a 10 cm gas cell with KBr windows. Electron impact mass spectra were performed on a Finnigan-MAT Model 312 mass spectrometer (IE, 70 eV). Elemental analyses were performed by Desert Analytics (Tucson, AZ). Azidotrimethylsilane (Aldrich 95%) was purified by distillation (50 °C/175 mm), and its purity was checked by NMR and gas-phase IR. $InCl_3$ and $InBr_3$ (Aldrich) were used as received.

**Synthesis of $Cl_2InN_3$.** To a solution of $InCl_3$ (5.0 g, 22.6 mmol) in diethyl ether was added $SiMe_3N_3$ (4.0 mL, 30 mmol) by syringe at room temperature. The solution was refluxed for 3 days, after which the solvent was removed by distillation to yield a colorless solid. The material was dried under dynamic vacuum for an additional 12 h to remove completely any coordinated solvent and eventually yield $Cl_2InN_3$ (4.3 g, 84%). IR (Nujol; cm$^{-1}$): 3357 (w), 2482 (w), 2132 (vs), 1248 (s), 690 (m), 574 (w), 385 (m). Anal. Calcd: C, 0; H, 0; N, 18.44. Found: C, 0.31; H, 0.14; N, 18.64.

**Synthesis of $Cl_2InN_3(C_5H_5N)_2$.** $Cl_2InN_3$ (1.0 g, 3.0 mmol) was combined with 20 mL of dry $C_5H_5N$ at room temperature. The suspension was heated at 40 °C for 1 h, during which time the solid dissolved. The solution was cooled to −20 °C to yield a crystalline, colorless solid which was collected in several crops by successively concentrating and cooling the solution. The crystals were isolated by filtration and dried under vacuum. Yield: 1.5 g, 90%. Mp: 280 °C. IR (Nujol; cm$^{-1}$): 3118−3000 (w), 2090 (vs), 2070 (vs), 1609 (s), 1445 (s), 1377, 1340, 1277 (w), 1214 (w), 1072−1013 (m), 761−634 (s), 432 (m), 343 (m). $^1H$ NMR ($CDCl_3$, 22 °C): $\delta$ 8.9 (m), 7.8 (m),

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and 7.4 (m) (resonances corresponding to the coordinated $C_5H_5N$). Anal. Calcd: C, 31.16; H, 2.59; N, 18.2. Found: C, 30.51; H, 2.21; N, 19.1. EIMS (*m*/*z*): 229 $[Cl_2InN_3]^+$, 165 [ClIn], 150 [ClIn], 80 $[C_5H_5N]^+$.

**Synthesis of $Cl_2InN_3(THF)_2$.** $Cl_2InN_3$ (1.0 g, 4.4 mmol) was combined with 50 mL of dry THF at room temperature. The solution was cooled to −20 °C to yield a colorless crystalline solid, which was collected in several crops by successively concentrating and cooling the solution. The crystals were filtered and dried under vacuum (1.32 g, yield 88%). Anal. Calcd: C, 25.87; H, 4.31; N, 11.32. Found: C, 25.60; H, 4.29; N, 12.23. $^1H$ NMR ($CDCl_3$, 22 °C): $\delta$ 1.9 and $\delta$ 3.9. IR (Nujol): 3369 (w), 2995−2903 (m), 2566 (w), 2115 (vs), 1345 (w), 1275 (s), 1182 (w), 1024 (s), 920 (m), 1015 (s), 855 (s), 685 (m), 605 (w), 350 (m).

**Synthesis of $Br_2InN_3$.** To a solution of $InBr_3$ (5.0 g, 14.0 mmol) in diethyl ether was added $SiMe_3N_3$ (3.75 mL, 28 mmol) by syringe at room temperature. The solution was refluxed for 4 days, during which time a light brown precipitate formed. The material was isolated by filtration, washed several times with ether, and dried 60−80 °C under high vacuum to remove any coordinated solvent in the solid. Yield: 1.5 g, 35%. Anal. Calcd: C, 0; H, 0; N, 13.29. Found: C, 1.09; H, 0.05; N, 12.71. IR (Nujol; $cm^{-1}$): 2121 (vs), 1257 (s), 678 (m), 581 (w). We attribute the organic impurity in the material to traces of residual solvent which is extremely hard to remove completely even by heating the samples under high vacuum. The discrepancy in the N content might be due to loss of $N_2$ from the $N_3$ group in the combustion analysis.

**X-ray Structure of $Cl_2InN_3(THF)_2$.** A suitable specimen was loaded into a 0.3 mm X-ray capillary and sealed under nitrogen. Data collection and refinement parameters are presented in Table 1. Systematic absences and diffraction symmetry are consistent with the space groups *Cmca* and *C2cb*. The *E*-statistics suggested the centrosymmetric option, which yielded chemically reasonable and computationally stable results of refinement. The structure was solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. A $\psi$-scan absorption correction was applied to the data. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. One of the THF molecules is partially, but unresolvably, disordered at C(1). One-fourth of the molecule located on a 2/*m* position comprises the asymmetric unit. All software and sources of the scattering factors are contained in the SHELTXTL (5.10) program library (G. Sheldrick, Siemens XRD, Madison, WI).

## Conclusion

The new inorganic indium azides $Cl_2InN_3$, and $Br_2GaN_3$ are obtained as colorless, nonvolatile, polymeric solids by reaction of the corresponding halides with $SiMe_3N_3$. The $Cl_2InN_3$ compound combines with THF and pyridine to form stable Lewis acid−base complexes with compositions $Cl_2InN_3(C_5H_5N)_2$ and $Cl_2InN_3(THF)_2$. The X-ray structure of $Cl_2InN_3(THF)_2$ consists of dinuclear units incorporating a planar $[Cl_2InN_3]_2$ framework in which the In atoms are connected by the $\alpha$-nitrogen of the azide groups to form a four-membered $In_2N_2$ heterocycle. This conformation is unique among group 13 azides, although similar structures containing $Ga_4N_4$ eight-membered and $B_3N_3$ six-membered rings have been observed for the tetramer $[HClGaN_3]_4$ and the trimer $[Cl_2BN_3]_3$, respectively.

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**Supporting Information Available:** X-ray crystallographic files in CIF fornat for the structure determination of $[Cl_2InN_3(THF)_2]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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