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THE CRYSTAL AND MOLECULAR STRUCTURE OF DIMETHYLINDIUM-PYRIDINE-2-CARBALDEHYDE OXIMATE $[\text{InMe}_2(\text{ON}=\text{CHC}_5\text{H}_4\text{N})]_2$

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Summary

Dimethylindium-pyridine-2-carbaldehyde oximate crystallises from benzene in the orthorhombic space group *Pbcn*, with cell dimensions a 33.15, b 9.54, c = 14.30 Å. The unit cell contains eight dimeric oximate molecules $[\text{InMe}_2(\text{ON}=\text{CHC}_5\text{H}_4\text{N})]_2$ and four molecules of benzene. Each oximate group coordinates through both its nitrogen atoms to one indium atom, and through its oxygen atom to the other indium atom of the dimer. The dimer thus consists of a row of five fused rings, two terminal pyridine rings, a central 6-membered InONInON ring, and two intervening 5-membered InNCCN rings (I). The indium atoms are 5-coordinate, and adopt a distorted trigonal bipyramidal geometry, in which the NInN "bite" of the oximate ligand is only 69° , and the axial In–N bonds to the pyridine nitrogen atoms (2.51 Å) are significantly longer than the equatorial In–N bonds to the oximate nitrogen atoms (2.28 Å). The ClInC angle between the bonds to the equatorial methyl groups averages 138° .

Introduction

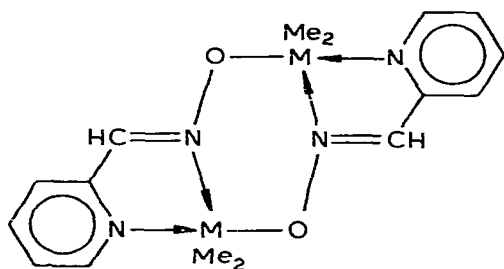
During studies of reactions between oximes and alkyl-Group III metal compounds [1,2], pyridine-2-carbaldehyde oxime, 2- $\text{C}_5\text{H}_4\text{NCH}=\text{NOH}$, was found to react with the trimethyls MMe_3 ($\text{M} = \text{Al, Ga, In or Tl}$) to form methane and $[\text{MMe}_2(\text{ON}=\text{CHC}_5\text{H}_4\text{N})]_2$ derivatives which were dimeric in benzene.

The fused-ring structure I was suggested for these derivatives on the basis of their infrared and ^1H NMR spectra. We here describe an X-ray crystallographic study of the indium compound, $[\text{InMe}_2(\text{ON}=\text{CHC}_5\text{H}_4\text{N})]_2$, which has confirmed structure I and revealed features that were not apparent from the spectroscopic studies.

A sample of dimethylindium-pyridine-2-carbaldehyde oximate was prepared

* Died August 4th, 1979.

from InMe_3 and $2\text{-C}_5\text{H}_4\text{NCH=NOH}$ in toluene below room temperature, and



(I)

recrystallized from benzene as very thin transparent plates with a faint yellow colour. Though hydrolysed by water, the crystals were sufficiently air-stable to allow data to be collected without the need to seal the crystals in glass tubes. The crystals were orthorhombic, space group $Pbcn$, with cell dimensions a 33.15(1), b 9.54(1), c 14.30(1) Å. The unit cell contains eight dimeric molecules $[\text{InMe}_2(\text{ON}=\text{CHC}_5\text{H}_4\text{N})]_2$ together with four molecules of benzene: $D_{\text{calc.}}$ 1.62 g cm^{-3} , $D_{\text{obs.}}$ 1.61 g cm^{-3} ; absorption coefficient for Mo- K_α radiation 20.5 cm^{-1} .

Data collection, structure solution and refinement

The crystal used for data collection was a very thin plate with well-developed $\{100\}$ faces, of dimensions 0.35 by 0.22 by 0.01 mm. Data were collected on a Hilger and Watts four circle diffractometer, using Zr-filtered Mo- K_α radiation. The length of the a axis necessitated a small scanning range for each reflection. An octant of the sphere of reflection up to $\theta = 20^\circ$ was collected for both the set of reflections hkl and the equivalent set $h\bar{k}l$. The data were corrected for Lorentz and polarisation effects but not for absorption. Altogether 2120 independent reflections were obtained, of which 1377 were classed as observed, having net counts $\geq 2\sigma$.

The coordinates of the indium atoms were determined by evaluation of the Patterson function, and improved through two cycles of least squares refinement to an R -value of 0.26. The structure factors based on the positions of the heavy atoms were then used to compute a Fourier map from which it was possible to assign positions to all the remaining atoms of the pyridine-2-carbaldehyde oximate molecules except the hydrogens. Three cycles of refinement, the first two isotropic, the third with anisotropic temperature parameters, reduced R to 0.094. A difference map then revealed extra peaks attributable to the molecules of benzene of crystallisation. Incorporating these in the refinement reduced the R value to 0.059, a value which could not be improved by including the ring hydrogen atoms in calculated positions.

Description and discussion of the structure

The structure of the dimeric molecule $[\text{InMe}_2(\text{ON}=\text{CHC}_5\text{H}_4\text{N})]_2$ is illustrated in Fig. 1. The arrangement of such molecules and of the benzene of crystallisa-

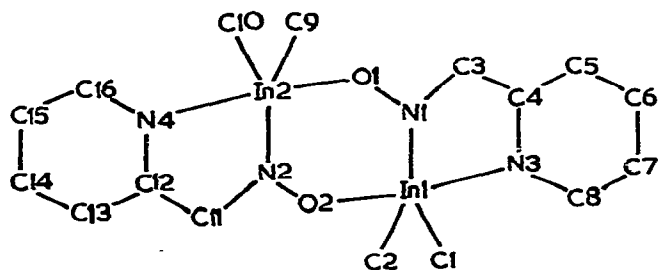


Fig. 1. The structure of dimethylindium-pyridine-2-carbaldehyde oximate dimer, $[\text{InMe}_2(\text{ON}=\text{CHC}_5\text{H}_4\text{N})]_2$, showing atom numbering.

tion within the crystal is shown in Fig. 2. The atomic coordinates, interatomic distances, bond angles and equations of some mean planes are given in Tables 1-4.

The molecular structure (Fig. 1) is of type I that had been inferred from spectroscopic studies [2], with five heterocyclic rings (two terminal pyridine rings, a central InONInON ring, and two intervening InNCCN rings). One feature that had not been inferred from the spectra, however, was the folded nature of the structure. If the molecule is divided into two halves by a line drawn through the oxygen atoms O(1) and O(2), the two halves are approximately planar and inclined to each other at an angle of ca. 55° .

The planarities of individual sections of the molecules are illustrated by the data in Table 4. The two pyridine rings are planar within experimental error. The atoms In(2), O(1), O(2) and N(2) are coplanar, though the corresponding

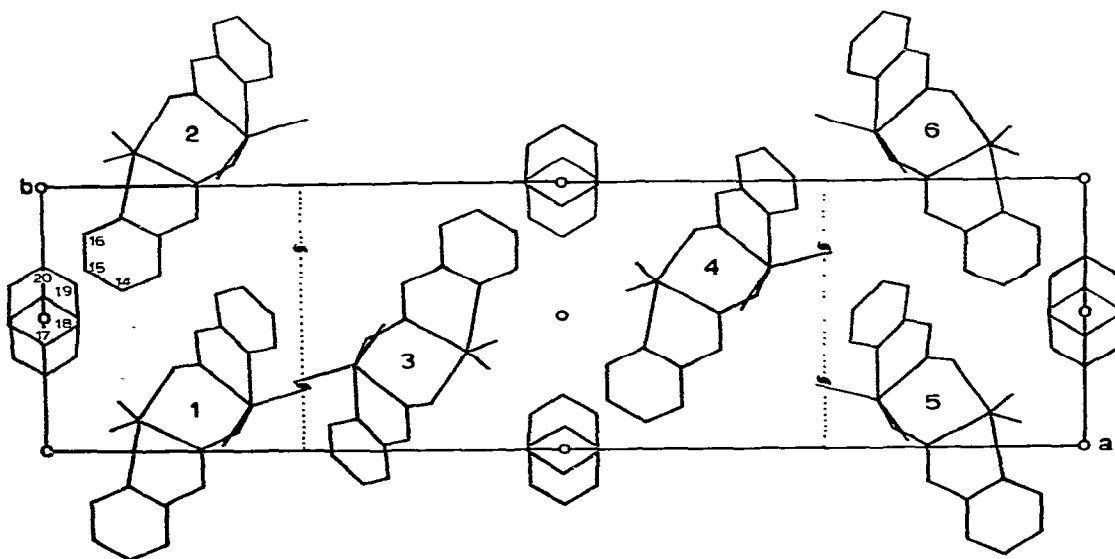


Fig. 2. The arrangement of the oximate and benzene molecules in the crystal of $[\text{InMe}_2(\text{ON}=\text{CHC}_5\text{H}_4\text{N})]_2 \cdot \frac{1}{2}\text{C}_6\text{H}_6$.

TABLE 1

POSITIONAL PARAMETERS ($\times 10^4$), WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES, FOR $[\text{InMe}_2(\text{ON}=\text{CHC}_5\text{H}_4\text{N})]_2 \cdot \frac{1}{2}\text{C}_6\text{H}_6$

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
In(1)	1993(1)	1745(2)	2164(1)
In(2)	0911(1)	1274(2)	0735(1)
O(1)	1266(4)	3215(15)	1014(10)
O(2)	1861(4)	0756(17)	0775(11)
N(1)	1511(5)	3353(16)	1763(11)
N(2)	1503(5)	0085(18)	0638(11)
N(3)	1990(5)	3757(17)	3285(12)
N(4)	0786(5)	-1211(19)	0228(14)
C(1)	2577(8)	2377(30)	1663(17)
C(2)	1706(8)	0222(26)	3070(16)
C(3)	1481(6)	4567(21)	2220(16)
C(4)	1732(7)	4757(20)	3035(15)
C(5)	1684(6)	5998(19)	3539(15)
C(6)	1940(7)	6222(25)	4307(15)
C(7)	2223(8)	5154(25)	4568(15)
C(8)	2245(7)	3956(25)	4022(14)
C(9)	0702(7)	1976(25)	-0593(16)
C(10)	0629(8)	0904(34)	2097(20)
C(11)	1518(7)	-1260(23)	0439(14)
C(12)	1133(7)	-1947(22)	0210(14)
C(13)	1145(9)	-3397(23)	0002(18)
C(14)	0783(9)	-4000(29)	-0275(21)
C(15)	0424(9)	-3201(29)	-0278(19)
C(16)	0433(8)	-1803(26)	-0045(21)
C(17) ^a	0000	4133(41)	2500
C(18) ^a	0344(84)	4920(33)	2198(21)
C(19) ^a	0324(8)	6379(30)	2196(20)
C(20) ^a	0000	7076(47)	2500

^a Atoms of the benzene of crystallisation.

set In(1), O(1), O(2) and N(1) are not. While the ring In(1), N(1), C(3), C(4) and N(3) is not quite planar, the planarity of the ring In(2), N(2), C(11), C(12) and N(4) can be accepted at the 1% probability level. The atoms In(1), N(1),

TABLE 2

INTERATOMIC DISTANCES (Å), AND THEIR ESTIMATED STANDARD DEVIATIONS (Å $\times 10^3$), IN $[\text{InMe}_2(\text{ON}=\text{CHC}_5\text{H}_4\text{N})]_2 \cdot \frac{1}{2}\text{C}_6\text{H}_6$

In(1)—O(2)	2.241(16)	In(2)—O(1)	2.229(14)
In(1)—N(1)	2.288(15)	In(2)—N(2)	2.271(16)
In(1)—N(3)	2.501(17)	In(2)—N(4)	2.514(19)
In(1)—C(1)	2.153(27)	In(2)—C(9)	2.129(24)
In(1)—C(2)	2.165(25)	In(2)—C(10)	2.190(28)
O(1)—N(1)	1.350(21)	O(2)—N(2)	1.361(22)
N(1)—C(3)	1.333(26)	N(2)—C(11)	1.316(28)
C(3)—C(4)	1.445(31)	C(11)—C(12)	1.471(31)
N(3)—C(4)	1.329(26)	N(4)—C(12)	1.349(28)
C(4)—C(5)	1.396(27)	C(12)—C(13)	1.416(31)
C(5)—C(6)	1.403(30)	C(13)—C(14)	1.389(40)
C(6)—C(7)	1.435(34)	C(14)—C(15)	1.412(41)
C(7)—C(8)	1.387(33)	C(15)—C(16)	1.375(38)
C(8)—N(3)	1.364(28)	C(16)—N(4)	1.356(32)

TABLE 3

BOND ANGLES ($^{\circ}$), AND THEIR ESTIMATED STANDARD DEVIATIONS ($^{\circ} \times 10$) in $[\text{InMe}_2(\text{ON}=\text{CHC}_5\text{H}_4\text{N})]_2 \cdot \frac{1}{2}\text{C}_6\text{H}_6$

O(2)—In(1)—N(1)	85.6(6)	O(1)—In(2)—N(2)	88.3(5)
O(2)—In(1)—N(3)	152.9(6)	O(1)—In(2)—N(4)	157.3(6)
O(2)—In(1)—C(1)	89.9(8)	O(1)—In(2)—C(9)	94.0(7)
O(2)—In(1)—C(2)	99.3(8)	O(1)—In(2)—C(10)	101.5(9)
N(1)—In(1)—N(3)	69.1(5)	N(2)—In(2)—N(4)	69.8(6)
N(1)—In(1)—C(1)	110.9(8)	N(2)—In(2)—C(9)	112.6(8)
N(1)—In(1)—C(2)	107.1(8)	N(2)—In(2)—C(10)	110.1(9)
N(3)—In(1)—C(1)	90.1(8)	N(4)—In(2)—C(9)	89.2(8)
N(3)—In(1)—C(2)	97.5(8)	N(4)—In(2)—C(10)	91.9(9)
C(1)—In(2)—C(2)	141.4(10)	C(9)—In(2)—C(10)	134.8(10)
In(2)—O(1)—N(1)	122.7(11)	In(1)—O(2)—N(2)	119.7(11)
In(1)—N(1)—O(1)	123.6(11)	In(2)—N(2)—O(2)	120.6(11)
In(1)—N(1)—C(3)	120.8(13)	In(2)—N(2)—C(11)	122.2(13)
O(1)—N(1)—C(3)	115.4(15)	O(2)—N(2)—C(11)	117.2(16)
In(1)—N(3)—C(4)	112.4(13)	In(2)—N(4)—C(12)	110.8(14)
In(1)—N(3)—C(8)	126.8(14)	In(2)—N(4)—C(16)	128.2(16)
N(1)—C(3)—C(4)	117.5(18)	N(2)—C(11)—C(12)	116.8(18)
N(3)—C(4)—C(3)	119.8(19)	N(4)—C(12)—C(11)	120.2(19)
C(3)—C(4)—C(5)	117.3(19)	C(11)—C(12)—C(13)	117.3(19)
C(4)—N(3)—C(8)	120.4(18)	C(12)—N(4)—C(16)	120.9(20)
N(3)—C(4)—C(5)	122.9(19)	N(4)—C(12)—C(13)	122.5(20)
C(4)—C(5)—C(6)	117.7(19)	C(12)—C(13)—C(14)	116.1(23)
C(5)—C(6)—C(7)	119.4(20)	C(13)—C(14)—C(15)	120.4(26)
C(6)—C(7)—C(8)	118.2(22)	C(14)—C(15)—C(16)	120.3(26)
C(7)—C(8)—N(3)	121.2(21)	C(15)—C(16)—N(4)	119.5(24)

TABLE 4

EQUATIONS OF MEAN PLANES, AND PERPENDICULAR DISTANCES (\AA) OF ATOMS THEREFROM, IN $[\text{InMe}_2(\text{ON}=\text{CHC}_5\text{H}_4\text{N})]_2 \cdot \frac{1}{2}\text{C}_6\text{H}_6$

Plane 1	$0.683X + 0.425Y - 0.549Z = 3.249$					
Atom	N(3)	C(4)	C(5)	C(6)	C(7)	C(8)
p	-0.01	0.02	-0.01	0.01	-0.01	0.02
Plane 2	$0.169X + 0.247Y - 0.945Z = -0.136$					
Atom	N(4)	C(12)	C(13)	C(14)	C(15)	C(16)
p	-0.02	0.03	-0.02	0.01	0.00	0.02
Plane 3	$0.672X + 0.591Y - 0.447Z = -4.041$					
Atom	In(1)	O(1)	O(2)	N(1)		
p	0.00	-0.06	0.04	0.09		
Plane 4	$0.044X + 0.186Y - 0.982Z = -0.671$					
Atom	In(2)	O(1)	O(2)	N(2)		
p	0.00	0.00	-0.01	0.01		
Plane 5	$0.676X + 0.463Y - 0.573Z = 3.462$					
Atom	In(1)	N(1)	N(3)	C(3)	C(4)	
p	0.00	-0.04	-0.04	0.05	0.03	
Plane 6	$0.099X + 0.264Y - 0.959Z = -0.388$					
Atom	In(2)	N(2)	N(4)	C(11)	C(12)	
p	0.00	0.03	0.03	-0.03	-0.02	
Plane 7	$0.200X + 0.532Y + 0.823Z = -4.754$					
Atom	In(1)	N(1)	C(1)	C(2)		
p	0.00	-0.02	-0.12	-0.10		
Plane 8	$0.475X + 0.849Y + 0.232Z = +2.708$					
Atom	In(2)	N(2)	C(9)	C(10)		
p	0.00	0.06	0.20	0.29		

C(1) and C(2) are non-planar, as are In(2), N(2), C(9) and C(10). If the indium atoms adopted undistorted trigonal bipyramidal geometries, with the oxygen atoms and pyridine nitrogen atoms in axial positions, each of these last two groups would be coplanar.

Each pyridine-2-carbaldehyde oximate group $\text{ON}=\text{CHC}_5\text{H}_4\text{N}$ is thus tridentate, chelating through both nitrogen atoms (though by no means equally strongly) to one indium atom, and bridging through oxygen to the second indium atom of the dimer. The "bite" of the ligand, as indicated by the angle $\text{N}(1)\text{In}(1)\text{N}(3)$ or $\text{N}(2)\text{In}(2)\text{N}(4)$, is small (69°). The difference (0.25 \AA) between the lengths of the two In—N bonds formed by each oximate group is striking. The oximate nitrogen atoms form bonds of a length (average 2.28 \AA) that may be regarded as normal for single In—N bonds (cf. 2.28 \AA in the octahedral complex $\text{bipyInCl}_2(\text{acac})$ [3] and 2.19 \AA for the sum of the tetrahedral covalent radii [4]). The bonds formed by the pyridine nitrogen atoms (average length 2.53 \AA) are clearly much weaker, and fall into the category of "secondary bonds" [5]. Significantly, they are opposite to the O—In bonds (the angles $\text{O}(2)\text{—In}(1)\text{—N}(3)$ and $\text{O}(1)\text{—In}(2)\text{—N}(4)$ average 155°).

The In—C and In—O bonds are of normal length for single bonds. For example, the average In—C distance of 2.16 \AA may be compared with values of 2.18 \AA in Me_2InCl [6], 2.17 \AA (average) in Me_2InBr [7], 2.10 \AA (average) in Me_2InOAc [8], 2.05 \AA in MeInCl_2 [9], 2.24 \AA in Cp_3In [10], 2.26 \AA in InMe_2^- [11], 2.23 \AA in InPh_4^- [11], 2.25 \AA in Et_2InOAc [12] and 2.13 \AA in $\text{Et}_2\text{InOScMe}$ [13]. The In—O distance of 2.24 \AA (average) in $[\text{InMe}_2(\text{ON}=\text{CHC}_5\text{H}_4\text{N})_2]$ may be compared with values of 2.24 \AA (average) and 2.26 \AA in the octahedral aquo complexes $\text{InCl}_3(\text{OH}_2)_2(\text{dioxan})_3$ [14] and $[\text{InCl}_4(\text{OH}_2)_2]^-$ [15] respectively, and lies at the upper end of the range $2.02\text{--}2.25 \text{ \AA}$ typical for In—O bonds in extended structures [16–19].

The indium atoms of $[\text{InMe}_2(\text{ON}=\text{CHC}_5\text{H}_4\text{N})_2]$ thus form four normal length bonds (to the two methyl carbon atoms and to the oximate nitrogen and oxygen atoms) and one long bond (to the pyridine nitrogen atom). The metal coordination may be regarded as distorted trigonal bipyramidal, the axial atoms being the oxygen and pyridine nitrogen atoms. Alternatively, the coordination may be regarded as derived from a tetrahedral arrangement of the four normal length bonds, distorted by bringing up the pyridine nitrogen into a "secondary bonding" [5] position in the CCN face as nearly opposite to the In—O bond as the $\text{ON}=\text{CHC}_5\text{H}_4\text{N}$ -ligand geometry allows. Whichever way one views the metal coordination, the bond angles at the metal clearly also reflect the tendency for the methyl groups, i.e. carbon atoms C(1), C(2), C(9) and C(10), to position themselves so as to minimise repulsive interactions with neighbouring non-bonded atoms. The methyl groups are the only terminally attached groups in the molecule. They project above and below the planes of the molecule and feature in several short non-bonding contacts (see Table 5) which clearly influence the angles $\text{C}(1)\text{In}(1)\text{C}(2)$ and $\text{C}(9)\text{In}(2)\text{C}(10)$.

Hausen et al. [7] have drawn attention to the linear relationship that apparently exists between the ClInC bond angle in various methylindium compounds and the difference, $\Delta\nu$, between the frequencies of their symmetric and asymmetric InC_2 stretching frequencies. The present compound has $\nu_{\text{asym}} 516 \text{ cm}^{-1}$, $\nu_{\text{sym}} 482 \text{ cm}^{-1}$ [2], $\Delta\nu 34 \text{ cm}^{-1}$ and an average ClInC bond angle of 138° .

TABLE 5

SELECTED INTRAMOLECULAR NON-BONDING DISTANCES (Å), AND THEIR ESTIMATED STANDARD DEVIATIONS ($\text{Å} \times 10^3$) IN $[\text{InMe}_2(\text{ON}=\text{CHC}_5\text{H}_4\text{N})]_2 \cdot \frac{1}{2}\text{C}_6\text{H}_6$

In(1)—C(8)	3.49(2)	C(2)—N(2)	3.54(2)
In(2)—C(16)	3.52(3)	C(2)—C(10)	3.89(4)
O(1)—O(2)	3.08(2)	C(9)—C(16)	3.80(3)
N(1)—B(2)	3.51(2)	C(10)—N(1)	3.77(3)
C(1)—C(8)	3.86(3)		

Though these figures support the thesis that $\Delta\nu$ decreases as the CInC bond angle decreases, use of Hausen's relationship would have led us to predict a CInC angle of ca. $125\text{--}130^\circ$ from the infrared data.

The packing of the oximate molecules and the benzene of crystallisation in the crystals is illustrated in Fig. 2. For purposes of clarity not all eight asymmetric units are shown on the projection. The relationship between the molecules that are shown are as follows: 2 is related to 1 by a unit cell translation along b ; 3 is related to 1 by the 2_1 screw axis; 4 is related to 3 by a centre of symmetry; 5 is related to 4 by the b glide plane (dotted line); and 6 is related to 5 by a unit cell translation along b .

The packing arrangement is such that two molecules of benzene lie in a sandwich arrangement with a separation of just over 7 \AA , the two molecules being related by a centre of symmetry. The pyridine ring consisting of atoms N(4) and C(12)—C(16) projects towards the middle of this sandwich and is approximately equidistant between the two benzene molecules. The (001) projection in Fig. 2 illustrates this arrangement showing the pairs of benzene molecules lying on the two fold rotation axis at $Z = \pm c/4$. The length of the dimer is approximately the same as the b axis, while the width permits four molecules to lie along the a axis.

The distorted trigonal bipyramidal geometry found in $[\text{InMe}_2(\text{ON}=\text{CHC}_5\text{H}_4\text{N})]_2$ thus adds a further example of this type of coordination among organoindium compounds. Earlier examples have included Me_2InCl [6], MeInCl_2 [9], $\text{Et}_2\text{InOScMe}$ [13], Me_3In [20] and Ph_3In [21]. Undistorted trigonal bipyramidal geometry is known elsewhere in indium chemistry, e.g. in the complex $\text{InCl}_3 \cdot 2\text{PPh}_3$ [22], as is one example of a tetragonal pyramidal arrangement of five ligands about indium, in $(\text{Et}_4\text{N})_2\text{InCl}_5$ [23].

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