

# Indium-Based Liquid Clathrates. II. Inclusion Compounds Derived from Salts of the Tetrachloroindate Anion, $\text{InCl}_4^-$ , and the Crystal Structure of $[\text{Li} \cdot 15\text{-c-5}] [\text{In}(\text{CH}_3)_3\text{Cl}]$ (15-c-5 = 15-crown-5)

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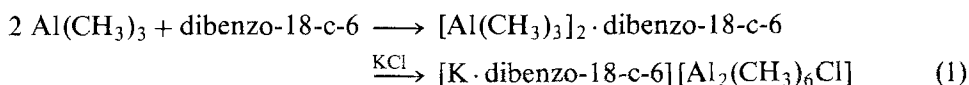
**Abstract.** Indium(III) chloride reacts with 12-c-4 to give the 1 : 1 adduct  $[\text{InCl}_3 \cdot 12\text{-c-4}]$ . This complex is a convenient In precursor to liquid clathrates.  $[\text{InCl}_3 \cdot 12\text{-c-4}]$  reacts with LiCl to form  $[\text{Li} \cdot 12\text{-c-4}] [\text{InCl}_4]$ . When the reaction is carried out in the presence of an aromatic solvent such as toluene, a liquid inclusion complex forms readily. It has been determined that the  $\text{C}_6\text{H}_5\text{CH}_3 : [\text{Li} \cdot 12\text{-c-4}] [\text{InCl}_4]$  ratio is 2. Alkylation of the 15-c-5 adduct of  $\text{InCl}_3$  with methyllithium yields  $[\text{Li} \cdot 15\text{-c-5}] [\text{In}(\text{CH}_3)_3\text{Cl}]$ . The salt fails to form inclusion complexes with aromatic molecules. This compound has been characterized using single crystal X-ray diffraction. The molecule belongs to the monoclinic space group  $P2_1/n$ , with  $a = 7.515(2)$ ,  $b = 18.952(6)$ , and  $c = 13.938(7)$  Å,  $\beta = 95.12(3)^\circ$  and  $D_{\text{calc}} = 1.43 \text{ g cm}^{-3}$  for  $Z = 4$ . Least squares refinement based upon 2348 observed reflections led to a final  $R = 0.039$ .

**Key words:** Liquid clathrate, indium, crystal structure, crown ether.

**Supplementary Data** relevant to this paper have been deposited with the British Library under number SUP82054 (20 pages).

## 1. Introduction

We recently reported the first liquid clathrates formed from aromatic molecules and the organoindium salt  $[\text{K} \cdot 18\text{-c-6}]_2[\text{In}_2(\text{CH}_3)_3\text{Cl}_2\text{I}_3]$  [1]. During the course of these studies it was found that the adduct  $(12\text{-c-4})\text{InCl}_3$  can be easily prepared and acts as an excellent precursor to purely inorganic liquid inclusion compounds of the type  $[\text{Li} \cdot 12\text{-c-4}] [\text{InCl}_4](\text{aromatic})_x$ . The chemistry leading to these complexes is analogous to that previously found in the trimethylaluminum systems where the crown ether adduct serves as an alkylaluminum transfer reagent to form the 2 : 1 precursor salt (1) [2, 3].



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Not all tetrasubstituted indates form inclusion complexes however. Alkylation of  $[\text{InCl}_3 \cdot 15\text{-c-5}]$  yields  $[\text{Li} \cdot 15\text{-c-5}][\text{In}(\text{CH}_3)_3\text{Cl}]$ . This compound forms a homogeneous solution in toluene. Its structure, as well as details of the formation of the  $[\text{InCl}_4]^-$  inclusion complexes, are presented below.

## 2. Experimental

All operations were carried out under an atmosphere of dry nitrogen. 1,2-Dimethoxyethane (DME) was dried over the ketyl of sodium benzophenone and freshly distilled before use. Benzene, pentane, and toluene were dried over  $\text{LiAlH}_4$  and distilled before use.

### 2.1. SYNTHESIS OF $[\text{InCl}_3 \cdot 12\text{-c-4}]$

Indium trichloride (2.53 g, 11 mmol) was mixed with 30 mL of DME. 12-c-4 (1.78 mL, 11 mmol) was slowly added. The reaction mixture was stirred for 2 h. The DME was removed *in vacuo*. The residue was extracted with 20 mL of toluene. The extract was filtered. The solid was washed with an additional 20 mL of toluene followed by 20 mL of pentane. It was dried *in vacuo*: yield 3.46 g (79%), mp 228–235 °C (decomp.). IR (Nujol mull): 1305(*m*), 1292(*m*), 1234(*s*), 1140(*vs*), 1074(*vs*), 1023(*vs*), 926(*s*), 906(*s*), 831(*vs*).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 3.49$ (*s*), 3.46(*s*); Anal. Calcd. for  $\text{C}_8\text{H}_{16}\text{O}_4\text{Cl}_3\text{In}$ : C, 24.15; H, 4.02 Found: C, 23.94; H, 4.23.

### 2.2. SYNTHESIS OF $[\text{Li} \cdot 15\text{-c-5}][\text{In}(\text{CH}_3)_3\text{Cl}]$

Indium trichloride (3.85 g, 17.5 mmol) was mixed with 30 mL of DME. 15-c-5 (3.5 mL, 17.5 mmol) was added. The mixture was stirred for 2 h. The DME was removed *in vacuo*. The white residue was washed with  $2 \times 30$  mL portions of  $\text{C}_6\text{H}_6$ . The washings were discarded. The residue was dried *in vacuo* and then remixed with 30 mL of diethyl ether. The mixture was cooled to  $-78$  °C. Methyl lithium (37.5 mL, 1.4 M in  $\text{Et}_2\text{O}$ ) was slowly added. The mixture was warmed to room temperature and stirred for 18 h. The ether was removed *in vacuo*. The white residue was extracted with 30 mL of benzene. The mixture was filtered. The solution was concentrated and pentane added to initiate crystallization. The compound was obtained as very air sensitive crystals in *ca.* 52% yield. The elemental composition was established by a single crystal X-ray diffraction experiment.

### 2.3. PREPARATION OF THE INCLUSION COMPLEX $[\text{Li} \cdot 12\text{-c-4}][\text{InCl}_4] \cdot (\text{C}_6\text{H}_5\text{CH}_3)_2$

$[\text{InCl}_3 \cdot 12\text{-c-4}]$  (1.0 g, 2.5 mmol) was added to 20 mL of toluene along with  $\text{LiCl}$  (0.11 g, 2.5 mmol). The mixture was brought to near reflux over 30 minutes. During this time all of the solids dissolved and two liquid layers resulted. The flask was cooled to room temperature. The inclusion complex was separated from the excess toluene. Prolonged evacuation gave the parent salt,  $[\text{Li} \cdot 12\text{-c-4}][\text{InCl}_4]$ , as an air stable off white solid in *ca.* 92% yield. Anal. Calcd. for  $\text{C}_8\text{H}_{16}\text{O}_4\text{Cl}_4\text{LiIn}$ : Cl, 32.27, Found Cl, 32.87.

2.4. X-RAY DATA COLLECTION AND STRUCTURE SOLUTION FOR  $[\text{Li} \cdot 15\text{-c-5}][\text{In}(\text{CH}_3)_3\text{Cl}]$ 

Single crystals were sealed in thin-walled glass capillaries under an inert atmosphere. Details of the data collection and other pertinent information are given in Table I. Structure solution was accomplished by methods which have been previously described [4]. The final values of the positional parameters are given in Table II.

## 3. Results and Discussion

Historically liquid clathrates have been of the type  $\text{M}[\text{Al}_2\text{R}_6\text{X}] \cdot (\text{aromatic})_x$  whose formation occurs readily by interacting aromatics with the 2 : 1 adduct  $\text{M}[\text{Al}_2\text{R}_6\text{X}]$ . It has traditionally been held that the anion in these precursor salts must possess an angular geometry in order for inclusion to occur [5]. This shape provides a separation of the charge from the largely organic portion. Recent work in our laboratories has shown that this is too simplistic a criterion for the liquid clathrate phenomenon.

$\text{EtAlCl}_2$  reacts directly with benzo-15-c-5 in toluene to form a liquid clathrate [6]. The parent salt has been shown to be  $[\text{AlCl}_2 \cdot \text{benzo-15-c-5}][\text{EtAlCl}_3]$  via X-ray diffraction. Intrigued by this interesting chemistry, we studied similar indium systems to see if they too would display disproportionation and inclusion complex formation.

$\text{InCl}_3$  reacts with 12-c-4 to form the 1 : 1 adduct  $[\text{InCl}_3 \cdot 12\text{-c-4}]$  in good yield. This material is a fairly air stable, poorly soluble solid. Extended reflux in toluene failed to produce an inclusion compound (2).



Table I. Crystal data and summary of data collection

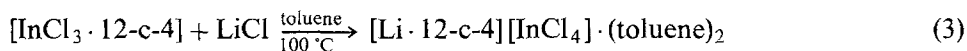
compd.	$\text{C}_{13}\text{H}_{29}\text{O}_5\text{ClIn}$
mol. wt.	422.63
space group	$P2_1/n$
cell constants	
<i>a</i> , Å	7.515(2)
<i>b</i> , Å	18.952(6)
<i>c</i> , Å	13.938(7)
β, deg	95.12(3)
cell vol Å <sup>3</sup>	1977
molecules/unit cell	4
ρ(calc), g cm <sup>-3</sup>	1.43
μ(calc), cm <sup>-1</sup>	13.35
radiation	MoKα
max crystal dimensions, mm	0.75 × 0.62 × 0.9
scan width	0.8 + 0.2 tan θ
standard reflections	400, 020, 002
variation of standards	<6%
reflections collected	3925
reflections with $I > 3\sigma(I)$	2348
no. of parameters varied	185
GOF	1.72
<i>R</i>	0.039
<i>R<sub>w</sub></i>	0.046

Table II. Final fractional coordinates and equivalent isotropic temperature factors

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eqv)
In	0.10119(7)	0.10878(3)	0.07789(4)	0.064
Cl	0.1487(3)	0.2417(1)	0.1114(2)	0.078
Li	-0.034(2)	0.3416(8)	0.066(1)	0.080
Me(1)	-0.047(1)	0.0800(5)	0.2031(6)	0.089
Me(2)	-0.067(1)	0.1081(6)	-0.0607(6)	0.110
Me(3)	0.387(1)	0.0782(5)	0.0769(8)	0.111
O(1)	0.127(2)	0.3850(9)	-0.047(1)	0.148
O(2)	-0.166(2)	0.3127(8)	-0.0659(9)	0.109
O(3)	-0.326(2)	0.3178(7)	0.087(1)	0.099
O(4)	-0.083(2)	0.3616(7)	0.223(1)	0.104
O(5)	0.127(2)	0.4361(7)	0.123(1)	0.092
C(1)	0.100(3)	0.357(2)	-0.132(1)	0.161
C(2)	-0.082(3)	0.331(1)	-0.146(1)	0.130
C(3)	-0.340(2)	0.295(1)	-0.075(1)	0.122
C(4)	-0.389(2)	0.272(1)	0.020(2)	0.110
C(5)	-0.331(3)	0.298(1)	0.180(2)	0.120
C(6)	-0.261(3)	0.360(2)	0.241(2)	0.154
C(7)	-0.012(3)	0.414(1)	0.268(1)	0.090
C(8)	0.141(4)	0.439(2)	0.220(2)	0.189
C(9)	0.268(2)	0.452(1)	0.070(2)	0.111
C(10)	0.215(3)	0.446(1)	-0.033(1)	0.108
O(1)A*	0.217(2)	0.4099(7)	0.034(1)	0.108
O(2)A	-0.034(2)	0.3702(7)	-0.0962(9)	0.094
O(3)A	-0.267(2)	0.2884(8)	-0.011(1)	0.111
O(4)A	-0.263(2)	0.339(1)	0.159(1)	0.162
O(5)A	0.017(2)	0.4188(9)	0.189(1)	0.141
C(1)A	0.235(3)	0.435(1)	-0.055(2)	0.137
C(2)A	0.131(3)	0.388(1)	-0.126(2)	0.157
C(3)A	-0.130(3)	0.316(1)	-0.147(2)	0.120
C(4)A	-0.312(4)	0.303(1)	-0.107(2)	0.130
C(5)A	-0.391(4)	0.268(2)	0.044(2)	0.206
C(6)A	-0.350(3)	0.272(1)	0.147(2)	0.152
C(7)A	-0.201(5)	0.343(2)	0.260(2)	0.196
C(8)A	-0.107(6)	0.411(2)	0.260(3)	0.223
C(9)A	0.198(3)	0.429(1)	0.206(2)	0.104
C(10)A	0.278(3)	0.450(1)	0.111(2)	0.146

\* The 15-crown-5 was disordered (50:50) just as has been noted in the structure of [Co(H<sub>2</sub>O)<sub>2</sub>(15-crown-5)](NO<sub>3</sub>)<sub>2</sub> [13].

If one adds a mole of LiCl, however, an inclusion complex forms immediately as evidenced by the complete dissolution of the [InCl<sub>3</sub>·12-c-4] and LiCl with concomitant formation of two liquid layers (3).



The liquid clathrate is quite stable at room temperature. The parent salt [Li·12-c-4][InCl<sub>4</sub>] will crystallize upon prolonged standing. As with all precursor salts, the addition of fresh toluene followed by brief heating results in the reformation of the inclusion complex. NMR integration provides a value of 2 for the aromatic to 'anion' ratio when toluene is used [7].

This complex is an important contribution to the study of liquid inclusion complexes. The liquid clathrate is formed from a purely inorganic precursor salt. A consequence of this is that the inclusion complex is air stable. Stability in air is a major improvement over the more traditional aluminum alkyl clathrates and offers promise of a wider range of potential applications.

In an attempt to extend the family of indate-derived liquid clathrates, we also studied the alkylation reaction (4).

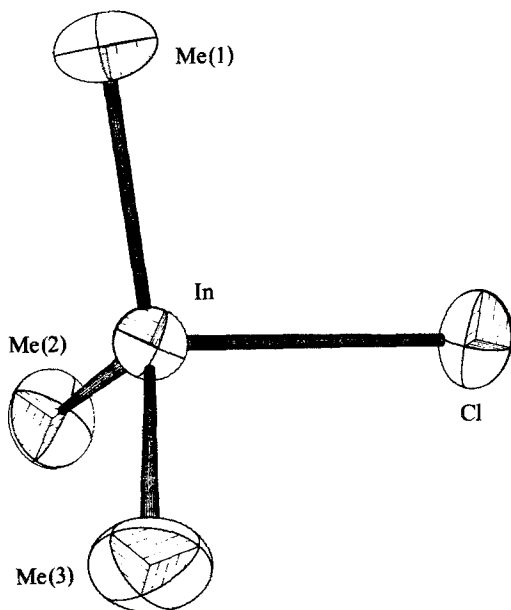
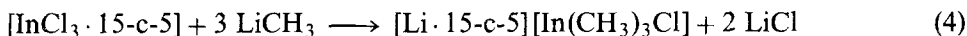


Fig. 1. View of the  $[\text{InMe}_3\text{Cl}]^-$  ion. Me = methyl carbon atom.

Table III. Selected bond distances (Å) and angles (°)

Atoms	Distance	Atoms	Distance
In—Cl	2.588(2)	In—Me(1)	2.224(9)
In—Me(2)	2.222(9)	In—Me(3)	2.232(9)
Cl—Li	2.40(1)	Li—O(1) <sup>a</sup>	2.24(2)
Li—O(2)	2.09(2)	Li—O(3)	2.29(2)
Li—O(4)	2.28(2)	Li—O(5)	2.27(2)
Atoms	Angle	Atoms	Angle
Cl—In—Me(1)	99.7(2)	Cl—In—Me(2)	102.9(3)
Me(1)—In—Me(2)	113.3(3)	Cl—In—Me(3)	97.9(3)
Me(1)—In—Me(3)	119.4(4)	Me(2)—In—Me(3)	118.2(4)
In—Cl—Li	131.1(3)		

<sup>a</sup> The 15-crown-5 was badly disordered, but the Li atom resides near the plane of the oxygen atoms and near the center of the crown (as evidenced by the small spread of Li—O distances).

[InCl<sub>3</sub>·15-c-5], prepared in an analogous manner to the 12-c-4 adduct, reacts with methyl lithium to give the chlorotrimethylindate salt. The structure of the anion is shown in Figure 1. Selected bond distances and angles are given in Table III.

The In—CH<sub>3</sub> distances vary from 2.222(9)–2.232(9) Å and agree well with other In—C(sp<sup>3</sup>) bond lengths: 2.239(8) Å in [HIn(CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>)<sub>3</sub>]<sup>−</sup> [8], 2.239(3) Å in K[In(CH<sub>3</sub>)<sub>4</sub>] [9]. The In—Cl distance is substantially longer than that found in other chloroindates: 2.37 Å in [InCl<sub>4</sub>]<sup>−</sup>, 2.398 Å in [(CH<sub>3</sub>)InCl<sub>3</sub>]<sup>−</sup> [10]. The geometry about the In shows a marked distortion from the tetrahedral, as evidenced by the variation in angles from 99.7(2) to 119.4(4)°. These angles agree well with those of the anion in [As(CH<sub>3</sub>)<sub>4</sub>][In(CH<sub>3</sub>)<sub>3</sub>Cl], 98.4–121.1° [11]. It is of interest to note that this organometallic indate fails to form an inclusion complex with aromatics.

It is obvious that the factors which dictate liquid clathrate formation are complex and offer the promise of interesting chemistry as these systems are studied in more detail. A future contribution will deal with the relation of these compounds to the room temperature molten salts [12].

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