Indium-Based Liquid Clathrates. I. The Preparation of the First Indium Liquid Inclusion Compound and Crystal Structure of its Parent Complex, $[K \cdot 18\text{-Crown-}6]_2[InClI_2(CH_3)][InClI(CH_3)_2]$

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Abstract. The synthesis of the first liquid clathrate derived from an indium precursor is described. The aromatic/anion ratio of the inclusion complex prepared using benzene is 12.4. The use of toluene results in the inclusion of 10.3 guest toluene molecules/anion. The crystal structure of the parent complex, $[K \cdot 18\text{-Crown-}6]_2[InClI_2(CH_3)][InClI(CH_3)_2]$ was carried out. The compound belongs to the monoclinic space group $P2_1/c$, with $a = 19.508(9)$, $b = 8.503(5)$, and $c = 29.437(9)$ Å, $\beta = 96.55(3)°$, and $D_{calc} = 1.83$ g cm^{-3} for $Z = 4$. Least-squares refinement based on 3449 observed reflections led to a final $R = 0.099$. The structure displays two different environments for the two K$^+$ cations in the asymmetric unit. One adopts the near-planar $[K \cdot 18\text{-crown-}6]^+$ configuration while the other K$^+$ resides 0.81 Å above the second 18-crown-6 plane. The latter K$^+$ is apparently pulled out of the crown by a strong interaction with a Cl$^-$ ion.

Key words: Liquid clathrate, indium, crystal structure, 18-crown-6.

1. Introduction

The interaction between organometallic salts and aromatic molecules has been extensively studied over the past several years [1]. The vast majority of the work has been conducted on host compounds of the type M[Al$_2$R$_6$X], where M is an alkali metal or tetraalkylammonium cation, R is a methyl or ethyl group, and X is a halide or pseudohalide anion. The organometallic precursor to these compounds has always been the trialkylaluminum, Al(CH$_3$)$_3$ or Al(C$_2$H$_5$)$_3$. Recently, liquid clathrates have been prepared from other aluminum compounds such as (C$_2$H$_5$)AlCl$_2$ and even AlCl$_3$ [2]. The other members of Group III, B-Tl, have largely been neglected. Trimethylgallium exhibits similar chemistry to its aluminum congener and several liquid clathrates based upon gallium have been prepared [3]. It is possible that thallium may be excluded from the traditional role in the anion, [Tl$_2$R$_6$X]$^-$, due to its preference for the 1$^+$ oxidation state. There has been no mention of using boron or indium complexes as precursors to liquid inclusion compounds.

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It is with this omission in mind that we have undertaken a study of indium chemistry and would like to report the preparation of the first indium-based liquid clathrate as well as a single crystal X-ray structure determination of a compound derived from it.

2. Experimental

All operations were carried out under an atmosphere of dry argon using standard Schlenk techniques. Diethyl ether was dried over the ketal of sodium benzophenone and freshly distilled before use. Benzene and toluene were dried over $LiAlH_4$ and freshly distilled before use.

2.1. SYNTHESIS OF $[K \cdot 18\text{-Crown-}6]_2[InClI_2(CH_3)][InClI(CH_3)_2]$

Indium trichloride (3.0 g, 13.5 mmol) was mixed with 30 ml of diethyl ether. Methyl lithium (29 ml, 1.4 M in Et_2O) was slowly added. The mixture was stirred at room temperature for 24 h. The ether was then removed *in vacuo* and the residue extracted with 30 ml of benzene. The benzene extract was filtered. Potassium iodide (1.12 g, 6.75 mmol) was added to the benzene solution along with 18-crown-6 (1.78 g, 6.75 mmol). The reaction was stirred at room temperature for 18 h. During this time the KI dissolved and two liquid layers resulted. Upon standing, air sensitive clear crystals precipitated from the lower layer in *ca.* 60% yield.

2.2. X-RAY DATA COLLECTION AND STRUCTURE SOLUTION FOR
$[K \cdot 18\text{-Crown-}6]_2[InClI_2(CH_3)][InClI(CH_3)_2]$
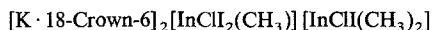
Single crystals were sealed in thin-walled glass capillaries under an inert atmosphere. Details of the data collection and other pertinent information are given in Table I. Structure solution was accomplished by methods which have been previously described [4]. The final values of the positional parameters are given in Table II.

Table I. Crystal data and summary of data collection

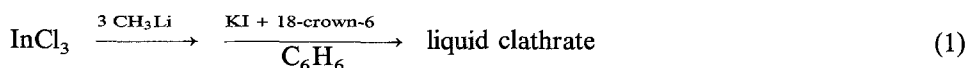| Compound	$C_{27}H_{57}In_2I_3K_2Cl_2O_{12}$	Radiation	$MoK\alpha$
Mol wt	1333.1	Max crystal dimensions, mm	$0.50 \times 0.50 \times 0.35$
Space group	$P2_1/c$	Scan width	$0.80 + 0.20 \tan\theta$
Cell constants		Standard reflections	800, 040, 0016
a, Å	19.508(9)	Variation of standards	$<3\%$
b, Å	8.503(5)	2θ range	2–42
c, Å	29.437(9)	Reflections collected	5887
β, deg	96.55(3)	Reflections with $I \cdot 3\sigma(I)$	3449
Cell vol, Å^3	4851	No. of parameters varied	373
Molecules/unit cell	4	GOF	1.25
ρ(calc), g cm^{-3}	1.83	R	0.099
μ(calc), cm^{-1}	32.0	R_w	0.111

3. Results and Discussion

The preparation of the In-based liquid clathrate was accomplished via a sequential set of reactions involving first alkylation of the indium(III) chloride followed by reaction with KI

Table II. Final fractional coordinates and equivalent isotropic temperature factors

Atom	x/a	y/b	z/c	U eq
In(1)	0.3657(2)	0.1249(4)	0.3505(1)	0.100(12)
I(1)	0.3339(2)	− 0.1889(4)	0.3288(1)	0.108(13)
I(2)	0.4688(2)	0.1054(6)	0.4174(2)	0.156(17)
Cl(1)	0.2649(4)	0.225(1)	0.3825(3)	0.058(9)
Me(1)	0.392(2)	0.243(5)	0.289(1)	0.095(27)
In(2)	0.8861(1)	0.4874(3)	0.47480(8)	0.061(4)
I(3)	0.7897(1)	0.4947(3)	0.39030(8)	0.066(7)
Me(2)	0.878(2)	0.250(5)	0.496(1)	0.038(7)
Me(3)	0.869(2)	0.714(5)	0.502(2)	0.134(20)
Cl(2)	0.9885(4)	0.513(1)	0.4334(3)	0.070(19)
K(2)	1.0502(3)	0.2922(8)	0.6573(2)	0.052(5)
C(1)	0.977(2)	0.624(4)	0.724(1)	0.070(9)
O(1)	1.044(1)	0.548(2)	0.7173(7)	0.061(21)
C(2)	1.090(2)	0.557(4)	0.759(1)	0.070(8)
C(3)	1.159(2)	0.491(4)	0.749(1)	0.071(16)
O(2)	1.148(1)	0.325(3)	0.7402(7)	0.058(10)
C(4)	1.212(2)	0.247(5)	0.735(1)	0.073(18)
C(5)	1.197(2)	0.071(5)	0.729(1)	0.071(9)
O(3)	1.153(1)	0.054(2)	0.6864(7)	0.060(14)
C(6)	1.141(2)	− 0.108(4)	0.676(1)	0.078(30)
C(7)	1.096(2)	− 0.114(4)	0.631(1)	0.085(10)
O(4)	1.030(1)	− 0.039(2)	0.6362(7)	0.065(14)
C(8)	0.983(2)	− 0.044(4)	0.596(1)	0.073(7)
C(9)	0.914(2)	0.011(4)	0.607(1)	0.059(15)
O(5)	0.921(1)	0.169(3)	0.6194(7)	0.056(8)
C(10)	0.857(2)	0.237(4)	0.628(1)	0.068(9)
C(11)	0.868(2)	0.413(4)	0.633(1)	0.063(5)
O(6)	0.916(1)	0.439(2)	0.6729(7)	0.056(15)
C(12)	0.932(2)	0.605(4)	0.679(1)	0.067(20)
K(1)	0.6331(4)	0.2987(9)	0.4118(2)	0.064(5)
O(7)	0.674(2)	− 0.017(4)	0.420(2)	0.165(91)
O(8)	0.640(2)	0.110(5)	0.331(1)	0.151(47)
O(9)	0.565(2)	0.394(6)	0.328(1)	0.140(62)
O(10)	0.561(2)	0.594(4)	0.405(2)	0.146(59)
O(11)	0.606(2)	0.467(6)	0.491(2)	0.201(18)
O(12)	0.688(2)	0.178(8)	0.499(1)	0.210(16)
C(13)	0.681(2)	− 0.084(6)	0.369(2)	0.116(16)
C(14)	0.631(3)	− 0.025(9)	0.329(2)	0.165(25)
C(15)	0.594(3)	0.182(7)	0.292(2)	0.129(18)
C(16)	0.586(3)	0.356(8)	0.294(2)	0.150(21)
C(17)	0.546(3)	0.569(8)	0.327(2)	0.141(20)
C(18)	0.526(4)	0.61(1)	0.365(3)	0.184(30)
C(19)	0.560(2)	0.650(6)	0.458(2)	0.117(15)
C(20)	0.624(4)	0.593(9)	0.497(2)	0.168(25)
C(21)	0.660(3)	0.406(7)	0.531(2)	0.130(19)
C(22)	0.666(3)	0.220(9)	0.530(2)	0.156(26)
C(23)	0.703(3)	− 0.010(7)	0.492(2)	0.116(17)
C(24)	0.720(3)	− 0.047(8)	0.445(2)	0.151(23)

and 18-crown-6 (1). This stoichiometry was chosen in order to synthesize an indium derivative analogous to the aluminum compounds $M[Al_2(CH_3)_6X]$.

$$InCl_3 \xrightarrow{\text{3 CH}_3\text{Li}} \xrightarrow[\text{C}_6\text{H}_6]{\text{KI + 18-crown-6}} \text{liquid clathrate} \qquad (1)$$

Reaction occurs readily at room temperature as evidenced by the dissolution of the KI and the concomitant formation of two liquid layers. Interestingly, no reaction occurs in the absence of the crown ether. This is yet another example of the use of crown ethers to synthesize liquid clathrates which are otherwise unobtainable [5]. When allowed to sit undisturbed, the lower phase precipitates large, air-sensitive crystals.

When the crystalline material is mixed with fresh aromatic solvent and warmed gently, the inclusion complex is again formed. If C_6H_6 is used as the solvent, the aromatic/anion ratio (A/A) of the resultant liquid clathrate is 12.4 [6]. The use of toluene results in an A/A of 10.3. The guest aromatic molecules freely travel across the interface between the two phases. By preparing a liquid clathrate using toluene, and replacing the upper layer with benzene, one can monitor this diffusion by ^{1}H NMR. After 18 h the A/A of the liquid clathrate was 11.6. The guest aromatic was comprised of *ca.* 84% C_6H_6 and 16% $C_6H_5CH_3$. Similar results have been obtained using Al-based liquid clathrates and a detailed study of the kinetics of this diffusion process has been carried out [7].

In order to better understand the nature of the In complex which serves as the precursor to the inclusion compound, we have undertaken a single crystal X-ray structure determination of the crystalline product. The structure of the indium parent complex is shown in Figure 1.
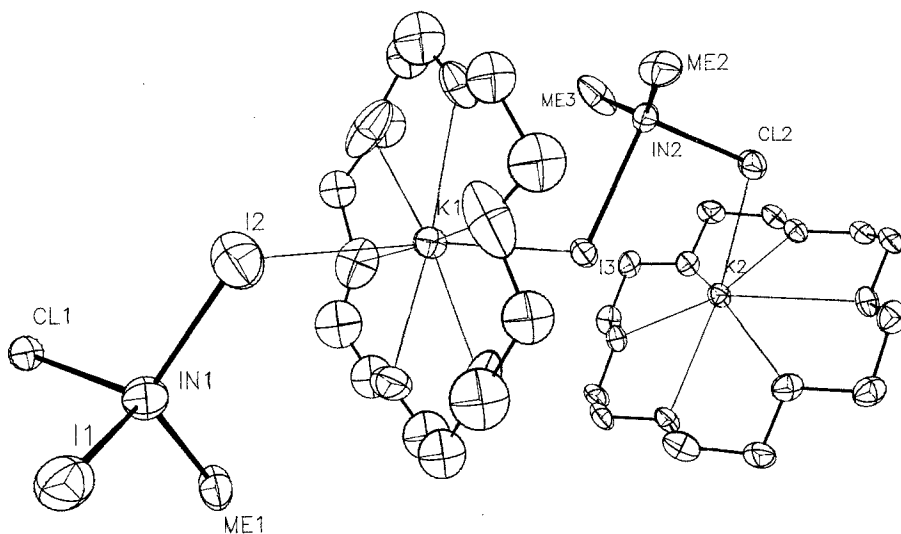

Fig. 1.   View of the independent cations and anions with the labelling scheme. Me = methyl carbon atom.

Important bond lengths and angles are given in Table III. $K(1)^+$ resides 0.23 Å out of the plane of the crown ether to which it is bound at an average $K\cdots O$ separation of 2.84 Å (range, 2.79(3)–2.88(3) Å). The two external contacts are to I(2) and I(3) at 3.623(9) and 3.600(8) Å, respectively. The rather symmetrical environment of $K(1)^+$ is further emphasized by the $I(2)\cdots K(1)\cdots I(3)$ angle of 172.4(2)°. K(2), on the other hand, lies 0.81 Å out of the plane of its crown ether. The $K\cdots O$ separation is 2.90 Å and the range, 2.82(2)–2.98(2) Å. The only other near-neighbor to $K(2)^+$ is Cl(2) at a contact of 3.16(1) Å [8]. This interaction has apparently pulled the K^+ out of the plane of the crown. It has been previously shown that potassium ions can be attracted by $K^+\cdots$aromatic interactions as far as 0.30 Å out of the plane of the bonded crown [9].

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

Atoms	Distance	Atoms	Distance
In(1)—I(1)	2.796(5)	In(1)—I(2)	2.655(5)
In(1)—Cl(1)	2.427(8)	In(1)—Me(1)	2.18(4)
In(2)—I(3)	2.943(3)	In(2)—Cl(2)	2.465(8)
In(2)—Me(1)	2.12(4)	In(2)—Me(3)	2.13(4)
K(1)···I(2)	3.623(9)	K(1)···I(3)	3.600(8)
K(2)···Cl(2)	3.16(1)		

Atoms	Angle	Atoms	Angle
I(1)—In(1)—I(2)	103.8(2)	I(1)—In(1)—Cl(1)	104.7(2)
I(2)—In(1)—Cl(1)	108.2(2)	I(1)—In(1)—Me(1)	109(1)
I(2)—In(1)—Me(1)	114.3(9)	Cl(1)—In(1)—Me(1)	116(1)
I(3)—In(2)—Cl(2)	93.2(2)	I(3)—In(2)—Me(2)	102(1)
Cl(2)—In(2)—Me(2)	109(1)	I(3)—In(2)—Me(3)	101(1)
Me(2)—In(2)—Me(3)	137(3)	Cl(2)—In(2)—Me(3)	106(2)
I(2)—K(1)—I(3)	172.4(2)		

The attraction of $K(2)^+$ for Cl(2) is further illustrated by the weaker In(2)—Cl(2) bond, as evidenced by the distance of 2.465(8) Å. The In(1)—Cl(1) distance is 2.427(8) Å, and even this is long for a terminal In—Cl bond. In $InCl_3[C(SiMe_3)_3] \cdot Li(THF)_3$ the two terminal In—Cl lengths are 2.367(7) and 2.389(6) Å, while the In—Cl···Li bridge distance is 2.432(6) Å [10]. The In—C distances, 2.14(4)–2.18(4) Å, are normal, but the In—I lengths present a puzzle. The two which interact with the K^+ ions are 2.655(5) and 2.943(3) Å, and the terminal one is 2.796(5) Å. The implication is that the bond between the two large atoms is weak enough to be subject to packing effects and to its environment in general.

Acknowledgements

References

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