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The reaction of $InCl_3$ with excess THF afforded the adduct $InCl_3(THF)_3$ in a good yield (77.1% based on $InCl_3$), and the X-ray crystal structure shows it to be a hexa-coordinated tris-adduct of indium(III) chloride. The crystal structure consists of discrete monomeric units with no abnormally short intermolecular separations. The geometry about the indium atom approximates to octahedral with the three chlorine atoms (mean In-Cl = 2.422 Å) and the oxygen atoms of each THF molecule (mean In-O = 2.254 Å) residing in the meridional conformation. Crystals of $InCl_3(THF)_3$ belong to the monoclinic space group $P\ 2_1/c$ with unit cell parameters a = 8.1863(2)Å, b = 12.5141(2) Å, c =16.815(4) Å, ß = 93.84(4)°, V = 1718.8(7) Å^3 for Z = 4. Full-matrix least-squares refinement based on 1603 reflections with $I > 2.5\sigma(I)$ converged at R = 0.062 (R_w = 0.084). IR spectroscopic measurements gave absorption bands near 1027 and 857 cm^{-1}, which are consistent with coordinated THF molecules. Variable temperature NMR studies showed that the tris-adduct was stable to disproportionation in solution between 20-60 °C.

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05 May 1994

SYNTHESIS AND CHARACTERIZATION OF A NEUTRAL SIX-COORDINATE TRIS-ADDUCT OF AN INDIUM(III) TRIHALIDE. X-RAY CRYSTAL STRUCTURE OF $InCl_3(THF)_3$.

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Abstract—The reaction of $InCl_3$ with excess THF afforded the adduct $InCl_3(THF)_3$ in a good yield (77.1% based on $InCl_3$), and the X-ray crystal structure shows it to be a hexa-coordinated tris-adduct of indium(III) chloride. The crystal structure consists of discrete monomeric units with no abnormally short intermolecular separations. The geometry about the indium atom approximates to octahedral with the three chlorine atoms (mean In-Cl = 2.422 Å) and the oxygen atoms of each THF molecule (mean In-O = 2.254 Å) residing in the meridional conformation. Crystals of $InCl_3(THF)_3$ belong to the monoclinic space group P $2_1/c$ with unit cell parameters a = 8.1863(2)Å, b = 12.5141(2) Å, c =16.815(4) Å, ß = 93.84(4)°, V = 1718.8(7) $Å^3$ for Z = 4. Full-matrix least-squares refinement based on 1603 reflections with $I > 2.5\sigma$ (I) converged at R = 0.062 (R_w = 0.084). IR spectroscopic measurements gave absorption bands near 1027 and 857 cm^{-1}, which are consistent with coordinated THF molecules. Variable temperature NMR studies showed that the tris-adduct was stable to disproportionation in solution between 20-60 °C.

Recent investigations in our laboratory[1] and that of Barron and co-workers[2] have shown that dehalosilylation is a facile means of forming the In-P bond. Thus, the latter obtained a product from the 1:1 mole ratio reaction of $InCl_3$ and $P(SiMe_3)_3$ at low temperature which was proposed to be $[Cl_2InP(SiMe_3)_2]_x$; whereas, we found that the 2:1 mole reaction at room temperature afforded $[Cl_2In_3P_3(SiMe_3)_2]_n$ and excess $InCl_3$ as the penta-coordinated bis-adduct $InCl_3(THF)_2$ (I).[3] Subsequent to the serendipitous isolation of I, a direct synthesis was attempted. It was found that the reaction of $InCl_3$ with excess THF afforded a six-coordinate compound $InCl_3(THF)_3$ **II** which is the tris-adduct. Compound **II** has been previously proposed by Fairbrother et al., but no solid-state structure was obtained.[4] They used colligative property measurements to postulate that the existence of **II** in the solid state would be of a lattice nature. We offer the solid-state structure and IR spectroscopic data which provide conclusive evidence that the three THF molecules present in the molecular structure are directly coordinated to the indium atom. In addition, to our knowledge, the crystal structure of **II** is one of the few examples of a neutral hexa-coordinated tris-adduct of an indium(III) trihalide with a meridional conformation (vide infra).

EXPERIMENTAL

Synthesis

All manipulations of air and moisture sensitive materials were performed in a Vacuum Atmospheres HE-493 Dri-Lab containing an argon atmosphere or by general Schlenk techniques. Toluene and THF were distilled from sodium benzophenone ketyl under dry dinitrogen. $InCl_3$ was purchased from Strem Chemicals and was used as received without further purification. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian XL-300 spectrometer operating at 300 and 75.4 MHz, respectively. ^1H and $^{13}C\{^1H\}$ spectra were referenced to TMS by using the residual protons or carbons of deuterated benzene at δ 7.15 or 128 ppm. NMR samples were prepared in 5-mm tubes under argon. IR spectroscopic data was collected on a BOMEM Michelson MB-100 Fourier Transform Infrared Spectrometer. A KBr pellet was prepared by adding 15 mg of **II** to 20 mg of KBr in an agate mortar and pestle with grinding to mix thoroughly. The sample transmittance was observed from 440-4000 cm^{-1}. Melting points (uncorrected) were obtained on a Thomas-Hoover Uni-melt apparatus and the melting point capillaries were flame-sealed under argon. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, NY. X-ray crystallographic data were obtained on a Rigaku AFC6/S diffractometer utilizing graphite-monochromated Mo-Kα radiation (λ = 0.71073Å) in the Single Crystal X-ray Structure Center at the University of North Carolina at Chapel Hill.

$InCl_3(THF)_3$ (**II**)

Inside a dry-box, a one-necked 200 cm^3 round-bottomed flask equipped with a reflux condenser, Teflon valve, and a stir-bar was charged with $InCl_3$ (0.659 g, 2.98 mmol) and 50 cm^3 of tetrahydrofuran. The mixture was removed from the dry-box and heated at reflux with stirring for 24 h under argon. The resulting clear solution was split into two equal portions in the dry-box. After diluting one portion with 2 cm^3 of toluene, both were cooled to -30 °C. After 3 days, colorless crystals of **II** (1.005 g total from both fractions, 77.1% yield based on $InCl_3$; m.p. = 59 - 62 °C) formed in both portions. Found: C, 32.73; H, 5.40. Calc. for $C_{12}H_{24}Cl_3InO_3$: C, 32.94; H, 5.53; IR (KBr, cm^{-1}) 3460 (vs), 1600 (vs), 1457 (w), 1027 (vs), 857 (vs); ^1H NMR: δ 1.26 (m, 4H, CH_2), 3.74 (m, 4H, O-CH_2). $^{13}C\{^1H\}$ NMR: δ 25.16 (s, CH_2), 69.20 (s, O-CH_2).

Variable temperature ^1H NMR

An internal standard of THF in degassed deuterated benzene was prepared by adding 0.02 cm^3 of THF to 0.06 cm^3 C_6D_6 in an NMR insert tube. A sample of **II** was prepared in an NMR tube by dissolving 16.9 mg of **II** in 0.6 cm^3 of C_6D_6. Individual

^1H spectra of the internal standard [δ 1.48 (m, 4H, CH_2), 3.52 (m, 4H, O-CH_2)] and of the internal standard inside the sample tube [δ 1.27 (m, 4H, CH_2), 1.47 (m,4H, CH_2), 3.52 (m, 4H, O-CH_2), 3.72 (m, 4H, O-CH_2)] were recorded at 19.5 °C. The internal standard was then removed and the sample tube was sealed with a rubber septum. The sample was heated in 5° increments over a temperature range from 19.5-59.5 °C, and a ^1H spectrum was recorded at each temperature [24.5 °C : δ 1.20 (m, 4H, CH_2), 3.72 (m, 4H, O-CH_2); 29.5 °C : 1.20 (m, 4H, CH_2), 3.73 (m, 4H, O-CH_2); 34.5 °C : 1.21 (m, 4H, CH_2), 3.73 (m, 4H, O-CH_2); 39.5 °C : 1.23 (m, 4H, CH_2), 3.73 (m, 4H, O-CH_2); 44.5 °C : 1.24 (m, 4H, CH_2), 3.73 (m, 4H, O-CH_2); 49.5 °C : 1.25 (m, 4H, CH_2), 3.73 (m, 4H, O-CH_2); 54.5 °C : 1.26 (m, 4H, CH_2), 3.74 (m, 4H, O-CH_2); 59.5 °C : 1.27 (m, 4H, CH_2), 3.74 (m, 4H, O-CH_2).

X-ray structural solution and refinement

Crystallographic data are summarized in Table I. The crystal used was a colorless block which was mounted on a glass fiber with a viscous oil under a stream of cold dinitrogen. X-ray intensity data were recorded at -170 °C, and the structure was solved by direct methods. Full-matrix least-squares refinement with weights based upon counter statistics was performed. Hydrogen atoms were incorporated at their calculated positions using a riders model in the later iterations of refinement which converged at $R = 0.062$ ($R_w = 0.084$). A final difference-Fourier synthesis revealed no unusual features (max. 1.28, min. -1.34 e $Å^{-3}$). Crystallographic calculations were performed using the NRCVAX[5] suite of structure determination programs. For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from ref. 6. Interatomic distances and angles are given in Table II. An ORTEP[7] diagram showing the solid-state conformation and atom numbering scheme of **II** is presented in Fig. 1. Full information concerning conditions for crystallographic data collection and structure refinement, atomic coordinates, thermal and positional parameters, and observed and calculated structure factors has been deposited with the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

Although there have been numerous examples of six-coordinate indium(III) trihalide compounds reported to date[8-12], an extensive review of the literature finds limited X-ray crystal analyses of such systems.[9-12] The principal methods for compound identification and structure elucidation have been Infrared and Raman spectroscopy, as well as colligative property measurements. Tris-adducts of indium(III) trihalides which have been crystallographically characterized are: [$InX_3L_3 \cdot Y_3$, X = Cl, Y= dioxane, L = H_2O (**III**)[9]; InX_3L_3, X = Cl, L = terpy (2, 2', 2''-terpyridyl) (**IV**)[10], Me_3PO (**V**)[11], Me_2SO (**VI**)[11], dmf (dimethylformamide) (**VII**)[12], dma (dimethylacetamide) (**VIII**)[12]; X = Br, L = Me_2SO (**IX**)[11]]. It is interesting to note that five of these seven (**V** - **IX**) were reported within the last five years.

The crystal structure of **II** consists of discrete monomeric units with the chlorine atoms and the THF oxygen atoms approximately octahedrally coordinated in a meridional conformation about the indium atom. Octahedral geometry is common to all of the above $InX_3 \cdot L_3$ adducts, however, **III** and **VI** - **VIII** are in the facial conformation. The Cl(1) - In - O(21) angle at 179.2(3)° in **II** deviates only slightly from an exactly linear value and is considerably greater than the mean Cl - In - Cl angle (166.7°) in **III**. The O(11) - In - O(31) and the Cl(3) - In - Cl(2) angles at 168.8(3)° and 169.5(1)°, respectively, evidence the degree of distortion from perfect octahedral symmetry. The mean In - Cl bond length at 2.421 Å in **II** is nearly identical to that of 2.422 Å in **III** and shorter than the corresponding lengths of 2.456 Å in **IV** and 2.435-2.608 Å in **V** - **VIII**. The In - O(21) bond in **II** at 2.304 Å, which is trans to Cl(1), is considerably longer than the In - O(11) [2.235(1) Å] and In - O(31) [2.223(1) Å] bonds. This bond lengthening may be attributed to steric interactions between the THF molecules or a trans-ligand influence where the donor ability of the Cl atom serves to weaken the In - O bond. The In - O bond lengthening is not observed, however, in **V** where the In - O bond lengths differ by only 0.007 Å. The two strong IR absorptions at 1027 and 857 cm^{-1}. correspond to the symmetric and asymmetric C-O-C stretching vibrations of the THF molecules and are near the values of 1011 and 850 cm^{-1} characteristic for coordinated THF molecules.[13] Fairbrother et al. used vapor pressure measurements on homogeneous unsaturated solutions of $InCl_3$ in THF to conclude that the bis-adduct **I** would predominate in solution, and that the tris-adduct **II** most likely exists only in the solid-state as a lattice compound. However, we concluded from variable temperature NMR studies that the tris-adduct is stable to disproportionation in deuterated benzene solution at temperatures ranging from 20-60 °C.

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Caption to Figure

Fig. 1. ORTEP diagram (30% probability ellipsoids) showing the solid-state conformation and atom numbering scheme of $InCl_3(THF)_3$ (II). The hydrogen atoms are represented by small circles.

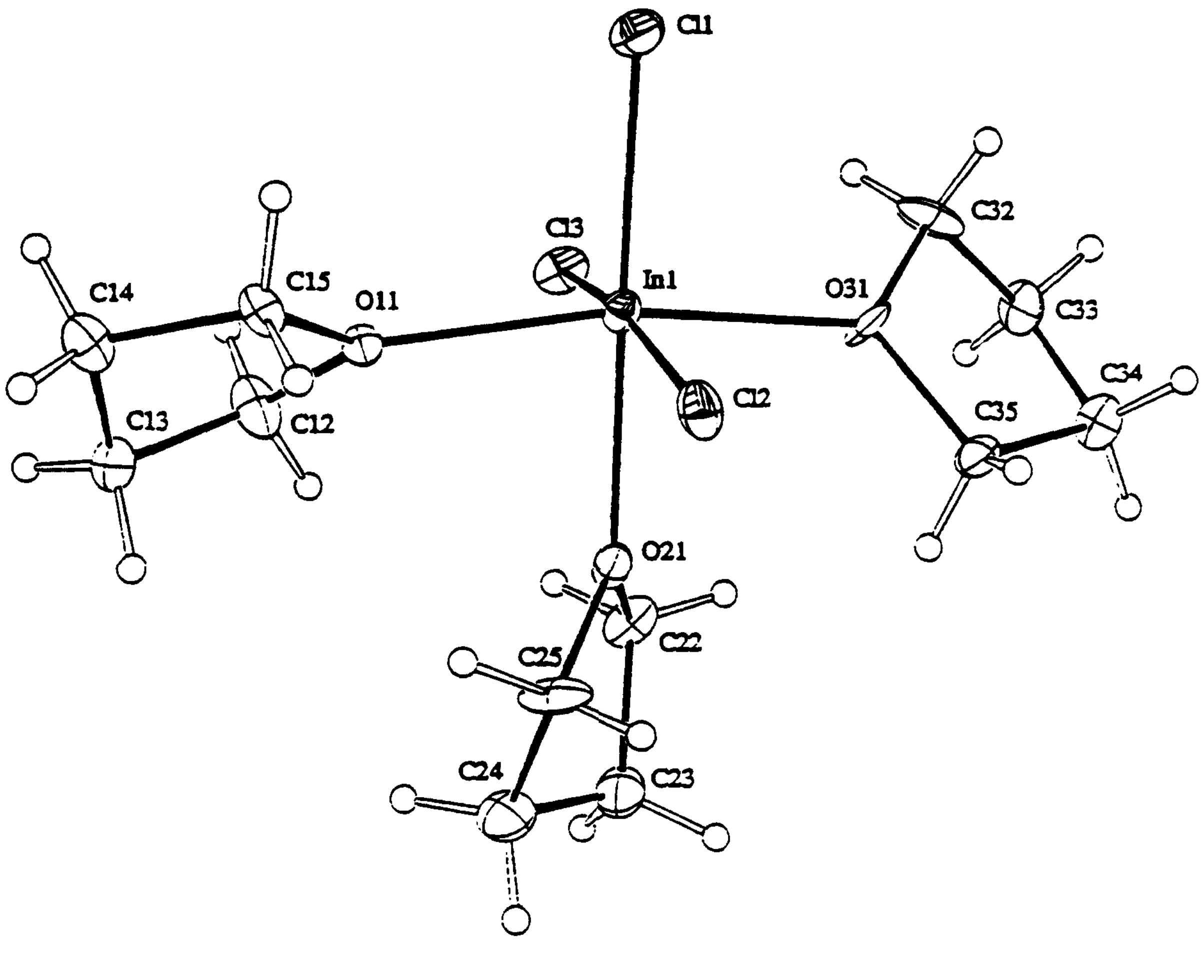
Cl1
C32
Cl3
In1
C14
C15
O11
O31
C33
C34
Cl2
C13
C12
C35
O21
C22
C25
C24
C23

Fig. 1

Table I. Crystallographic Data and Measurements for $InCl_3(THF)_3$ (**II**)

	II
molecular formula	$C_{12}H_{24}Cl_3InO_3$
formula weight	437.49
crystal system	monoclinic
space group	$P\,2_1/c$
a, Å	8.1863(2)
b, Å	12.5141(2)
c, Å	16.815(4)
β, deg	93.84(4)
V, $Å^3$	1718.8(7)
Z	4
radiation (wavelength, Å)	Mo-Kα (0.71073)
μ, cm^{-1}	18.3
temp, °C	-170
D_{calcd}, g cm^{-3}	1.691
crystal dimens., mm	0.30 x 0.30 x 0.30
T_{max}; T_{min}	1.00:0.37
scan type	ω
scan width, deg	1.00
Θ_{max}, deg	45
no. of rflns recorded	3401
no. of non-equiv. rflns recorded	2251
R_{merg} (on I)	0.063
no. of rflns retained, $I > 2.5\sigma(I)$	1603
no. of params. refined	173
R; R_w[a]	0.062; 0.084

Table I (continued)

	II
goodness-of-fit[b]	2.27
max shift / esd. in final least-squares cycle	0.002
final max, min $\Delta\rho$, e/Å^{-3}	1.280; -1.340

[a]$R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $R_w = [\Sigma w (|F_o| - |F_c|)^2/\Sigma w |F_o|^2]^{1/2}$.

[b]Goodness-of-fit = $[\Sigma w\Delta^2/(N_{observations} - N_{parameters})]^{1/2}$.

Table II. Interatomic Distances (Å) and Angles (°) for $InCl_3(THF)_3$ (II), with Estimated Standard Deviations in Parentheses

In(1)-Cl(1)	2.423(4)	O(21)-C(22)	1.412(2)
In(1)-Cl(2)	2.422(4)	O(21)-C(25)	1.500(2)
In(1)-Cl(3)	2.420(4)	C(22)-C(23)	1.546(2)
In(1)-O(11)	2.235(1)	C(23)-C(24)	1.56(3)
In(1)-O(21)	2.304(9)	C(24)-C(25)	1.487(2)
In(1)-O(31)	2.223(1)	O(31)-C(32)	1.454(2)
O(11)-C(12)	1.497(2)	O(31)-C(35)	1.494(2)
O(11)-C(15)	1.446(2)	C(32)-C(33)	1.436(2)
C(12)-C(13)	1.50(3)	C(33)-C(34)	1.566(2)
C(13)-C(14)	1.536(2)	C(34)-C(35)	1.480(2)
C(14)-C(15)	1.503(2)		

Cl(1)-In(1)-Cl(2)	94.65(1)	O(11)-C(12)-C(13)	104.2(1)
Cl(1)-In(1)-Cl(3)	95.57(1)	C(12)-C(13)-C(14)	103.0(1)
Cl(1)-In(1)-O(11)	98.1(3)	C(13)-C(14)-C(15)	101.8(1)
Cl(1)-In(1)-O(21)	179.2(3)	O(11)-C(15)-C(14)	108.5(1)
Cl(1)-In(1)-O(31)	93.1(3)	In(1)-O(21)-C(22)	128.5(9)
Cl(2)-In(1)-Cl(3)	169.52(1)	In(1)-O(21)-C(25)	122.4(7)
Cl(2)-In(1)-O(11)	91.69(2)	C(22)-O(21)-C(25)	108.6(1)
Cl(2)-In(1)-O(21)	84.99(2)	O(21)-C(22)-C(23)	108.4(1)
Cl(2)-In(1)-O(31)	87.7(3)	C(22)-C(23)-C(24)	99.2(1)
Cl(3)-In(1)-O(11)	89.2(3)	C(23)-C(24)-C(25)	103.4(2)
Cl(3)-In(1)-O(21)	84.77(2)	O(21)-C(25)-C(24)	105.1(1)
Cl(3)-In(1)-O(21)	82.6(3)	In(1)-O(31)-C(35)	127.6(9)
O(11)-In(1)-O(31)	168.8(3)	C(32)-O(31)-C(35)	108.8(1)
O(21)-In(1)-O(31)	86.2(4)	O(31)-C(32)-C(33)	103.6(1)
In(1)-O(11)-C(12)	124.8(8)	C(32)-C(33)-C(34)	103.8(1)
In(1)-O(11)-C(15)	127.5(8)	C(33)-C(34)-C(35)	102.0(1)
C(12)-O(11)-C(15)	107.7(1)	O(31)-C(35)-C(34)	105.6(1)