absorption measurements further into the near-infrared region.

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Supplementary Material Available: Table of observed and calculated structure factors (2 pages). Ordering information is given on any current masthead page.

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Preparation and Molecular Structure of Bis[2-[(dimethylamino)methyl]phenyl]chloroindium(III), a Five-Coordinate Diorganoindium Complex

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The neutral complex L_2InCl (L = 2-[(dimethylamino)methyl]phenyl) is the only product isolated from the reaction between $InCl_3$ and LiL in diethyl ether. The absolute configuration has been established by a complete three-dimensional X-ray diffraction study. The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 9.351$ (1) Å, $b = 10.411$ (2) Å, $c = 19.092$ (4) Å, and $V = 1858.7$ Å^3. Diffraction data were collected with a Syntex $P2_1$ automated diffractometer using graphite-monochromatized Mo Kα radiation. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations; final discrepancy indices are $R_F = 0.015$ and $R_{wF} = 0.022$ for 1729 observed reflections. The crystal structure shows that the molecule has distorted trigonal-bipyramidal stereochemistry with an InC_2Cl equatorial plane (In–Cl = 2.465 (1) Å, In–Cl(1) = 2.144 (3) Å, In–C(21) = 2.154 (3) Å) and apical In–N bonds (In–N(1) = 2.442 (Å) and In–N(2) = 2.482 (2) Å).

Introduction

X-ray crystallographic studies are now providing an increasing amount of information on the stereochemical properties of the coordination compounds of indium(III). Most of the inorganic structures which have been determined have proven to be tetrahedral (e.g., $InCl_4^-$),[1] octahedral ($InCl_6^{3-}$),[2] or substitution derivatives of these stereochemistries such as $[InI_2(Me_2SO)_4]^+$ (Me_2SO = dimethyl sulfoxide),[3] $[InCl_4(H_2O)_2]^-$,[4] or $[InCl_5(H_2O)]^-$.[5] This field was reviewed[6] in 1975, and a discussion of the structural results for neutral and anionic chloro complexes has been given elsewhere.[2] Only two five-coordinate indium(III) compounds have been identified by X-ray methods, although a number of such structures have been proposed on the basis of spectroscopic or other evidence. The neutral adduct $InCl_3 \cdot 2Ph_3P$ has D_{3h} symmetry in the coordination kernel with apical phosphine ligands.[7] The anion $InCl_5^{2-}$ has a square-based pyramidal structure,[8] and while there has been some discussion about the details of this structure,[9] it is clear that the stereochemistry differs markedly from those of the isoelectronic neighbors $CdCl_5^{3-}$ and $SnCl_5^-$, which have D_{3h} symmetry.[10,11]

Distorted trigonal-bipyramidal geometries have been observed by X-ray techniques for a number of triorgano- [$(CH_3)_3In$[12] and $(C_6H_5)_3In$[13]], diorgano- [$(C_2H_5)_2InOSC(CH_3)$[14] and $(CH_3)_2In(ON{=}CHC_5H_4N)$[15]], and organoindium compounds [$(CH_3InCl_2)_2$].[16] For each of these compounds pentacoordination results from intermolecular association. We now report the structure of bis[2-[(dimethylamino)methyl]phenyl]chloroindium(III) as the first example of an organoindium compound which has a trigonal-bipyramidal geometry as a result of intramolecular coordination. The preparation and molecular structure determination of this compound are described below. Other related preparative work and dynamic NMR studies of the solution behavior will be discussed elsewhere.

Experimental Section

Preparative Data. When freshly prepared [2-[(dimethylamino)methyl]phenyl]lithium (0.22 mol) in diethyl ether was added dropwise to a suspension of indium(III) chloride (24.0 g, 0.11 mol) in the same solvent (100 cm^3), an exothermic reaction lasting about 45 min occurred and a brown suspension formed. The reaction mixture was stirred for 24 h at room temperature, after which the suspended solid was collected by filtration. This solid was extracted with 3 × 100 cm^3 of benzene; when the volume of the bulk washings was reduced to 50 cm^3 by distilling off the solvent, a white solid was obtained, which was collected, washed with cold petroleum ether (bp 30–60 °C) and

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Table I. Summary of Crystal Data, Intensity Collections, and Structural Refinement for $InCl[(CH_3)_2NCH_2C_6H_4]_2$

cell constants[a] at 22 (1) °C	$a = 9.351$ (1), $b = 10.411$ (2), $c = 19.092$ (4) Å
cell vol	1858 (1) $Å^3$
space group	$P2_12_12_1$ (D_2^4; No. 19)
Z	4
mol wt	418.7
ρ(calcd)	1.497 g cm^{-3}
diffractometer	Syntex $P2_1$
radiatn	Mo Kα ($\lambda = 0.71069$ Å)
monochromator	highly oriented graphite
cryst faces and dimens (from centroid, in mm)	(001), 0.120; $(00\bar{1})$, 0.120; (101), 0.158; $(\bar{1}0\bar{1})$, 0.158; $(\bar{1}01)$, 0.158; $(10\bar{1})$, 0.158; $(0\bar{1}1)$, 0.140; $(01\bar{1})$, 0.140; $(0\bar{1}1)$, 0.140; (011), 0.140
abs coeff (μ)	13.96 cm^{-1}
transmissn coeff	0.69–0.76
2θ range	3–50°
scan type	coupled θ(crystal)–2θ(counter)
scan width	1.0° below Kα_1 to 1.0° above Kα_2
scan speed	variable, 2.02–4.88°/min
total bkgd time/scan time	0.5
total no. reflctns measd (including std reflctn)	3317; *hkl* (3–50° complete) 2069, $hk\bar{l}$ (3–50° partial) 1298
unique avgd data (NO)	1729; a total of 2797 ($F_o > 3\sigma(F_o)^2$) avgd
$F_o^2 > 3\sigma(F_o)^2$	$R(I) = 2.2\%$
no. of variables (NV)	219
R_F; R_{wF}; GOF	1.48%; 2.21%; 0.8
std reflctns, max dev	3 measured every 39 reflections: $\bar{2}$,2,14, 9%; $36\bar{1}$, 8%; $45\bar{8}$, 12%

[a] Unit cell parameters were derived from a least-squares fit to the setting angles ($\pm 2\theta$, $\pm\omega$, χ, ϕ) of the unresolved Mo Kα components of the reflections $\{163\}$, $\{18\bar{3}\}$, $\{2,2,\bar{14}\}$, $\{\bar{3},1,11\}$, $\{3\bar{3}\bar{9}\}$, $\{\bar{3}6\bar{1}\}$, $\{\bar{3}74\}$, $\{\bar{4}58\}$, $\{\bar{5}1\bar{5}\}$, $\{543\}$, $\{\bar{6}17\}$, $\{64\bar{1}\}$, $\{7\bar{1}5\}$, and $\{\bar{7}22\}$.

dried in vacuo. Further quantities of this material were obtained by again reducing the volume of the benzene extract solution and adding petroleum ether. The total yield of colorless crystalline bis[2-[(dimethylamino)methyl]phenyl]chloroindium(III) was 32.0 g (77%). Anal. Calcd for $C_{18}H_{24}InClN_2$: In, 27.4; Cl, 8.48. Found: In, 27.6; Cl, 8.39.

The same compound, L_2InCl, can also be prepared by a redistribution reaction between L_3In and $InCl_3$ in diethyl ether at room temperature.[17] No evidence for the formation of $LInCl_2$ was obtained in this experiment.

Crystallographic Measurements. A suitable crystal with well-defined faces was selected for data collection. The crystal was attached to the end of a thin glass fiber with epoxy, with the longest dimension approximately parallel to the fiber axis, and mounted on a Syntex $P2_1$ four-circle automated diffractometer under the control of a Nova 1200 computer. The diffractometer, at a takeoff angle of 6.1°, was equipped with a molybdenum X-ray tube and a highly oriented graphite monochromator ($\lambda = 0.71069$ Å, $2\theta_m = 12.2°$) and operated at 50 kV and 20 mA.

The crystal was optically centered in a random orientation. Determination of preliminary cell parameters, orientation matrix, and crystal quality were carried out by previously described techniques.[18] Examination of the ω scans of several low-angle-centered reflections showed no defects in the crystals; full peak width at half-height was less than 0.2°. The three axial photographs which were taken about each of the three chosen axes of the cell displayed *m* symmetry and confirmed the orthorhombic system; all three axes selected were found, by inspection, to be true solutions rather than submultiples of the true axial lengths. A unique set of data in the shell defined by $20° < 2\theta < 35°$ was next collected at a fast scan rate (29.3°/min). A set of 15 strong reflections, listed in Table I, widely separated in the reciprocal space, was chosen from these data and formed the basis for the determination of accurate cell parameters and the orientation matrix.

Intensity data were now collected via a θ(crystal)–2θ(counter) scan in 96 steps using bisecting geometry. The scan was from [2θ(Mo Kα_1(0.70926 Å)) − 1.0°] to [2θ(Mo Kα_2(0.71354 Å)) + 1.0°]. Backgrounds were measured both at the beginning and at the end of the scan, each for 25% of the time of the scan. The stability of the system and the crystal was monitored by measuring three strong check reflections after every 39 data; the intensities of these reflections decreased by approximately 10% during the course of data collection, and this was allowed for by appropriate scaling. During data collection any step of the scan which exceeded 5000 counts was subjected to a linear correction for coincidence losses. This correction is valid to about 5000 counts/interval; five reflections (011, 013, 102, 111, and 200) had greater magnitude and were remeasured, along with the three monitor reflections, at 30 kV and 15 mA.

An examination of the data revealed systematic absences (*h*00, $h = 2n + 1$; 0*k*0, $k = 2n + 1$; 00*l*, $l = 2n + 1$) consistent with the space group $P2_12_12_1$ (D_2^4; No. 19). Data were corrected for absorption, Lorentz, and polarization effects. [The *Lp* factor for a monochromator in the equatorial mode is given by

$$Lp = \frac{0.5}{\sin 2\theta}\left[\left(\frac{1 + (\cos^2 2\theta_m)(\cos^2 2\theta)}{1 + \cos^2 2\theta_m}\right) + \left(\frac{1 + |\cos 2\theta_m| \cos^2 2\theta}{1 + |\cos 2\theta_m|}\right)\right]$$

This equation assumes that the graphite-monochromator crystal is 50% mosiac and 50% perfect. The monochromator angle, $2\theta_m$, is 12.2° for Mo Kα radiation.] Details of the crystal and intensity data collection are provided in Table I.

Solution and Refinement of the Structure. All calculations were performed on the Amdhal computer at Wayne State University and the IBM 3031 at the University of Windsor. Programs used during the structural analysis include local versions of CHECK (check reflection by P. W. R. Corfield), PROC (data reduction by W. Schmonsees), FORDAP (Fourier synthesis by A. Zalkin), ORFLS (structure factor calculations and full-matrix least-squares refinement by W. Busing, K. Martin, and H. Levy), ORFEE (calculation of distances and angles with esd's by Busing, Martin, and Levy), HFINDER (hydrogen atom position calculation by A. Zalkin), ORTEP (thermal ellipsoid plotting program by C. K. Johnson), and XANADU (librational analysis by P. Roberts and G. M. Sheldrick). Scattering factors, including anomalous dispersion, and correction terms ($\Delta f'$) and ($\Delta f''$) for In and Cl atoms were taken from ref 19.

The positions of indium and chlorine atoms were determined from a sharpened three-dimensional Patterson synthesis; the positions of remaining nonhydrogen atoms were determined on the heavy-atom phases and difference Fourier syntheses. The structure was refined by full-matrix least-squares methods. The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, and the "ignorance factor" used was $p = 0.05$; in the initial stages of refinement, unit weights were used, and in the final stages, weights were derived from the counting statistics. Three cycles of full-matrix least-squares refinement of the positional and thermal parameters of the nonhydrogen atoms (all anisotropic) converged at $R_F = \sum||F_o| - |F_c||/\sum|F_o| = 0.027$. A difference Fourier synthesis then showed electron density maxima in most of the plausible hydrogen atom locations. Thereafter, all hydrogen atoms were included in idealized positions with C–H = 0.95 Å, HCH = 109.5°, and CCH = 120°; methyl hydrogen atoms were refined as a group, and isotropic thermal parameters were refined for all the hydrogen atoms. In three further cycles of refinement, convergence was achieved with $R_F = 0.015$ and $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.022$. The GOF $= \sum(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})$ was 0.80. In the final cycle of refinement, the largest shift/error ratio was 0.1 for the *x* coordinate of C(18). The absolute configuration was established from the final R_{wF} values for the two hands: for the other hand, the final R_{wF} was 0.030, as compared to $R_{wF} = 0.022$ for the structure given below. The final difference map had no features

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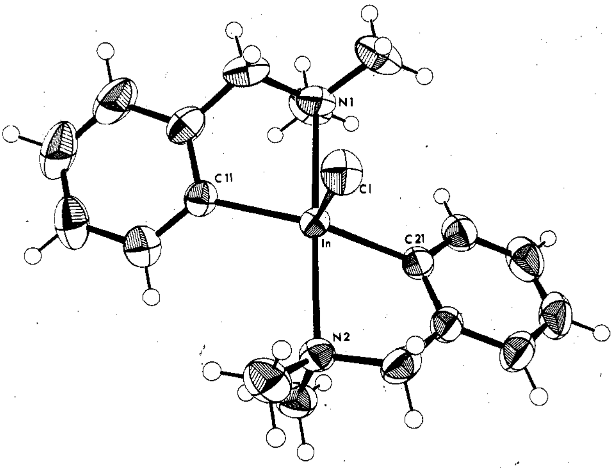

Figure 1. Stereochemistry of $InCl[(CH_3)_2NCH_2C_6H_4]_2$: ORTEP-II diagram, 50% probability ellipsoids for all atoms other than hydrogens, which are drawn for clarity as arbitrary spheres of 0.01-Å radius.

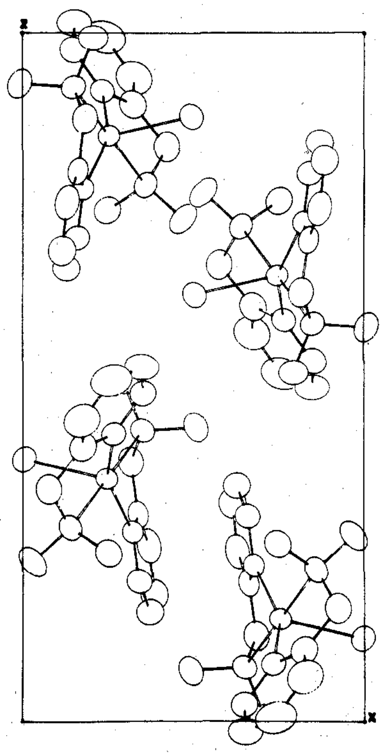

Figure 2. Packing of $InCl[(CH_3)_2NCH_2C_6H_4]_2$ in the unit cell. Hydrogen atoms have been omitted for clarity.

of chemical significance; the highest peak was 0.16 e Å^{-3} at 0.169, 0.263, 0.311. The function $\sum w(|F_o| - |F_c|)^2$ showed no appreciable dependence either upon $(\sin \theta)/\lambda$ or upon $|F_o|$, so that the weighting scheme is acceptable. There was no evidence for secondary extinction.

A table of observed and calculated structure factor amplitudes is available as supplementary data. Positional and thermal parameters are given in Tables II and III.

Results and Discussion

The X-ray analysis of $InCl[(CH_3)_2NCH_2C_6H_4]_2$ shows that the crystal consists of discrete monomeric units separated by normal van der Waals contacts (see Figures 1 and 2 and Table IV; least-squares planes of interest are given in Table V). There are two topics of especial interest in the structure, namely, the coordination kernel around the central indium atom and the stereochemistry of the chelating ligand.

The geometry of the molecule is essentially trigonal bipyramidal (TBP) with the two nitrogen atoms in apical and the chlorine and two carbon atoms in equatorial positions, which is the arrangement generally observed for TBP molecules containing two organic ligands.[20] The N_2InCl part of the molecule approaches ideal TBP geometry with an N(1)–In–N(2) angle of 178.4° and Cl–In–N(1) and Cl–In–N(2) angles of 89.4 (1) and 89.9 (1)°. The main distortion arises from the displacement of C(11) and C(21) from the equatorial plane. The geometric constraints of the NC_3In five-membered chelate ring dictate that in the presence of a collinear N–In–N arrangement, C(11) and C(21) will reside above the below the ideal equatorial plane [C(11)–In–N(1) = 77.0 (1)° and C(21)–In–N(2) = 76.1 (1)°]. The bite of the $2\text{-}((CH_3)_2NCH_2)C_6H_4$ ligand (L) is close to that observed in other [2-[(dimethylamino)methyl]phenyl]metal complexes, e.g., in $(C_6H_5)_2LSnBr$ (75.3 (4)°),[21] $CpTiL_2$ (73.4 (2)°),[22] and CpTiL (73 (1)°).[23] The geometry of the chelate rings is very similar

Table II. Atomic Coordinates and Thermal Parameters for $InCl[(CH_3)_2NCH_2C_6H_4]_2$[a]

	x	y	z
In	0.24595 (2)	0.21702 (2)	0.35194 (1)
Cl	0.00408 (8)	0.29581 (8)	0.37999 (5)
N(1)	0.1398 (3)	0.0475 (3)	0.2805 (2)
N(2)	0.3507 (3)	0.3939 (2)	0.4224 (1)
C(11)	0.2660 (3)	0.0503 (3)	0.4171 (2)
C(12)	0.3515 (4)	0.0344 (4)	0.4763 (2)
C(13)	0.3481 (5)	−0.0782 (4)	0.5150 (2)
C(14)	0.2588 (7)	−0.1769 (4)	0.4949 (3)
C(15)	0.1728 (5)	−0.1635 (4)	0.4362 (3)
C(16)	0.1761 (4)	−0.0501 (3)	0.3977 (2)
C(17)	0.0764 (4)	−0.0335 (4)	0.3363 (2)
C(18)	0.0297 (4)	0.0917 (4)	0.2310 (2)
C(19)	0.2520 (5)	−0.0259 (3)	0.2433 (2)
C(21)	0.3224 (3)	0.3511 (3)	0.2746 (2)
C(22)	0.3408 (4)	0.3311 (4)	0.2027 (2)
C(23)	0.3724 (4)	0.4321 (5)	0.1582 (2)
C(24)	0.3850 (4)	0.5547 (5)	0.1838 (2)
C(25)	0.3703 (4)	0.5761 (4)	0.2545 (2)
C(26)	0.3386 (3)	0.4754 (3)	0.3001 (2)
C(27)	0.3163 (4)	0.5038 (3)	0.3768 (2)
C(28)	0.2930 (4)	0.4129 (4)	0.4935 (2)
C(29)	0.5078 (4)	0.3776 (4)	0.4271 (2)

	x	y	z	B, Å^2
H(12)	0.4129	0.1025	0.4906	5 (1)
H(13)	0.4074	−0.0878	0.5550	6 (1)
H(14)	0.2559	−0.2544	0.5211	11 (2)
H(15)	0.1107	−0.2315	0.4225	5 (1)
H(22)	0.3325	0.2471	0.1841	6 (1)
H(23)	0.3846	0.4158	0.1096	8 (1)
H(24)	0.4040	0.6241	0.1531	10 (2)
H(25)	0.3823	0.6606	0.2721	5 (1)
H(171)	0.0558	−0.1161	0.3173	5 (1)
H(172)	−0.0094	0.0052	0.3521	6 (1)
H(271)	0.3755	0.5740	0.3896	6 (1)
H(272)	0.2188	0.5262	0.3839	4 (1)
H(181)	−0.0463 (52)	0.1334 (46)	0.2552 (27)	8.3 (8)
H(182)	0.0001 (52)	0.0174 (46)	0.2096 (27)	
H(183)	0.0648 (52)	0.1522 (46)	0.1958 (27)	
H(191)	0.2118 (38)	−0.1013 (39)	0.2229 (18)	5.9 (6)
H(192)	0.3246 (38)	−0.0502 (39)	0.2755 (18)	
H(193)	0.2919 (38)	0.0261 (39)	0.2075 (18)	
H(281)	0.1924 (41)	0.4254 (39)	0.4909 (22)	6.3 (6)
H(282)	0.3370 (41)	0.4859 (39)	0.5132 (22)	
H(283)	0.3124 (41)	0.3394 (39)	0.5217 (22)	
H(291)	0.5520 (36)	0.4529 (32)	0.4461 (17)	5.1 (5)
H(292)	0.5451 (36)	0.3624 (32)	0.3817 (17)	
H(293)	0.5265 (36)	0.3070 (32)	0.4565 (17)	

[a] Estimated standard deviations in parentheses.

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Table III. Anisotropic Thermal Parameters[a] for $InCl[(CH_3)_2NCH_2C_6H_4]_2$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
In	2.98 (1)	2.38 (1)	2.69 (1)	−0.14 (1)	−0.12 (1)	0.09 (1)
Cl	3.52 (3)	4.14 (3)	4.04 (3)	0.70 (3)	0.45 (3)	0.23 (3)
N(1)	3.2 (1)	3.6 (1)	4.1 (1)	−0.2 (1)	−0.6 (1)	−0.9 (1)
N(2)	3.7 (1)	2.8 (1)	3.4 (1)	0.1 (1)	−0.4 (1)	−0.3 (1)
C(11)	3.6 (1)	2.6 (1)	3.3 (1)	0.5 (1)	0.2 (1)	−0.0 (1)
C(12)	4.3 (1)	3.9 (1)	4.0 (1)	0.9 (1)	0.2 (1)	−0.0 (1)
C(13)	7.5 (2)	4.9 (2)	4.2 (2)	2.1 (2)	−0.1 (2)	1.2 (2)
C(14)	10.6 (3)	3.3 (2)	6.5 (2)	0.9 (2)	1.3 (3)	1.9 (2)
C(15)	8.1 (2)	2.6 (1)	7.0 (2)	−0.9 (2)	0.9 (2)	0.3 (2)
C(16)	4.5 (2)	2.6 (1)	5.0 (2)	−0.2 (1)	0.5 (1)	0.1 (1)
C(17)	4.1 (1)	3.7 (2)	5.7 (2)	−1.2 (1)	−0.1 (1)	−1.0 (1)
C(18)	4.6 (2)	5.5 (2)	5.4 (2)	0.8 (2)	−2.1 (2)	−1.6 (2)
C(19)	4.4 (1)	5.0 (2)	4.7 (1)	1.2 (2)	−0.5 (2)	−1.9 (1)
C(21)	2.7 (1)	3.7 (1)	3.2 (1)	−0.3 (1)	−0.1 (1)	0.6 (1)
C(22)	3.9 (1)	5.0 (2)	3.6 (1)	−0.2 (1)	−0.2 (1)	0.5 (1)
C(23)	4.7 (2)	8.2 (3)	4.1 (2)	−1.0 (2)	0.0 (1)	2.3 (2)
C(24)	4.7 (2)	6.3 (2)	5.7 (2)	−0.9 (2)	−0.2 (2)	3.4 (2)
C(25)	3.6 (1)	3.7 (2)	7.5 (3)	−0.8 (1)	−0.9 (2)	2.2 (2)
C(26)	2.6 (1)	3.3 (1)	4.6 (2)	−0.0 (1)	−0.5 (1)	1.0 (1)
C(27)	4.0 (1)	2.4 (1)	5.6 (2)	−0.0 (1)	−0.3 (1)	−0.0 (1)
C(28)	5.4 (2)	5.1 (2)	3.7 (1)	0.4 (1)	−0.1 (1)	−1.1 (2)
C(29)	3.7 (1)	4.2 (2)	5.4 (2)	−0.2 (1)	−1.0 (1)	−0.2 (1)

[a] The anisotropic thermal parameter is defined by the following expression: $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

to that observed in $CpTiL_2$,[22] $(C_6H_5)_2LSnBr$,[21] and the *C*-methyl-substituted analogue of this last compound,[24] with In, C(11), C(16), C(17) and In, C(21), C(26), C(27) being almost coplanar, and distinct puckering occurring at the C(17)–N(1)–In and C(27)–N(2)–In part of the chelate rings.

The C(11)–In–C(21) angle (153.3 (1)°) is quite large (cf. the C–In–C values of 141.4 (10) and 134.8 (10)° in $[InMe_2(ON{=}CHC_5H_4N)]_2$[15]) with the Cl–In–C(11) and Cl–In–C(21) angles being correspondingly small (102.9 (1) and 103.7 (1)°). The In–C bonds will be considerably more covalent than the In–Cl bond, and a value larger than 120° is therefore to be expected on electron-pair-repulsion arguments alone. However, the constraints of the NC_3In chelate ring in combination with the collinear N–In–N arrangement will also impose a widening of the C–In–C angle. While it is not surprising that the two nitrogen atoms occupy apical sites (cf. the structure of related organotin complexes[25]), it is not clear why a linear N–In–N arrangement with a bent equatorial plane is preferred over a structure with a bent N–In–N skeleton and strictly planar $ClInC_2$ trigonal plane. It is hoped that a planned X-ray study of other $XInL_2$ complexes, including those in which X = CH_3 or C_6H_5, will shed light on this question.

Table IV. Interatomic Distances (Å) and Angles (Deg) for $InCl[(CH_3)_2NCH_2C_6H_4]_2$[a]

(a) Bonding Distances

In–Cl	2.465 (1)		
In–N(1)	2.442 (3)	In–N(2)	2.482 (2)
In–C(11)	2.144 (3)	In–C(21)	2.154 (3)
N(1)–C(17)	1.482 (5)	N(2)–C(27)	1.473 (4)
N(1)–C(18)	1.472 (5)	N(2)–C(28)	1.473 (4)
N(1)–C(19)	1.479 (5)	N(2)–C(29)	1.482 (4)
C(11)–C(12)	1.395 (5)	C(21)–C(22)	1.400 (5)
C(11)–C(16)	1.391 (5)	C(21)–C(26)	1.391 (5)
C(12)–C(13)	1.386 (6)	C(22)–C(23)	1.383 (6)
C(13)–C(14)	1.379 (7)	C(23)–C(24)	1.372 (7)
C(14)–C(15)	1.386 (7)	C(24)–C(25)	1.373 (6)
C(15)–C(16)	1.392 (5)	C(25)–C(26)	1.395 (5)
C(16)–C(17)	1.507 (6)	C(26)–C(27)	1.507 (6)

(b) Angles

CL–In–N(1)	89.4 (1)	Cl–In–N(2)	89.9 (1)
Cl–In–C(11)	102.9 (1)	Cl–In–C(21)	103.7 (1)
N(1)–In–N(2)	178.4 (1)	C(11)–In–C(21)	153.3 (1)
N(1)–In–C(11)	77.0 (1)	N(2)–In–C(11)	104.6 (1)
N(1)–In–C(21)	102.7 (1)	N(2)–In–C(21)	76.1 (1)
In–N(1)–C(17)	99.9 (2)	In–N(2)–C(27)	99.8 (2)
In–N(1)–C(18)	114.6 (2)	In–N(2)–C(28)	117.0 (2)
In–N(1)–C(19)	110.7 (2)	In–N(2)–C(29)	109.9 (2)
C(17)–N(1)–C(18)	111.1 (3)	C(27)–N(2)–C(28)	111.1 (3)
C(17)–N(1)–C(19)	109.6 (3)	C(27)–N(2)–C(29)	109.9 (3)
C(18)–N(1)–C(19)	110.4 (3)	C(28)–N(2)–C(29)	108.8 (3)
In–C(11)–C(12)	128.0 (2)	In–C(21)–C(22)	128.1 (3)
In–C(11)–C(16)	113.6 (2)	In–C(21)–C(26)	113.5 (2)
C(12)–C(11)–C(16)	118.3 (3)	C(22)–C(21)–C(26)	118.0 (3)
C(11)–C(12)–C(13)	121.3 (4)	C(21)–C(22)–C(23)	121.0 (4)
C(12)–C(13)–C(14)	119.7 (4)	C(22)–C(23)–C(24)	120.4 (4)
C(13)–C(14)–C(15)	120.1 (3)	C(23)–C(24)–C(25)	119.5 (4)
C(14)–C(15)–C(16)	120.0 (4)	C(24)–C(25)–C(26)	120.9 (4)
C(11)–C(16)–C(15)	120.6 (4)	C(21)–C(26)–C(25)	120.2 (3)
C(11)–C(16)–C(17)	119.7 (3)	C(21)–C(26)–C(27)	120.5 (3)
C(15)–C(16)–C(17)	119.6 (4)	C(25)–C(26)–C(27)	119.3 (3)
C(16)–C(17)–N(1)	112.1 (3)	C(26)–C(27)–N(2)	113.0 (3)

[a] Librational analysis of rigid-molecule motion using XANADU showed a correction of 0.006, 0.005, and 0.004 Å for In–Cl, In–N, and In–C, respectively. The corrections for bonds not involving indium were negligible, in the range 0.002–0.003 Å. Estimated standard deviations are in parentheses.

The In–Cl bond distance 2.465 (1) Å is within the range reported for a number of inorganic In(III) complexes (cf. $InCl_5^{2-}$ 2.415 (12), 2.456 (7) Å;[8] $[InCl_4(H_2O)_2]^-$ 2.485 (2), 2.433 (3), 2.417 (3) Å[4]). Comparison with neutral adducts shows that the In–Cl bond in the present structure is somewhat longer than in $InCl_3{\cdot}2Ph_3P$ (2.377 (5), 2.382 (5), and 2.391 (5) Å[7]) but close to those in octahedral $InCl_3{\cdot}terpy$ (2.396 (1), 2.465 (1), and 2.507 (1) Å) (terpy = 2,2′,6′,2″-terpyridine)[26] and $[InCl_2(bpy)(acac)]$ (2.394 (1) and 2.443 (1) Å).[27] In organoindium compounds, the In–Cl values of 2.400 (1) and 2.384 (1) Å reported for $(CH_3InCl_2)_2$ (strongly distorted TBP)[16] are in the same range, but considerably higher values (2.673 (9), 2.954 (6), and 3.450 (9) Å) were found for [(C-

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Table V. Least-Squares Planes[a] and Atomic Deviations (Å) Therefrom for $InCl[(CH_3)_2NCH_2C_6H_4)]_2$

(a) $-0.3819X - 0.5685Y - 0.7287Z = -7.0518$
In, 0.006; Cl, −0.001; C(11), −0.003; C(21), −0.003

(b) $0.0166X + 0.5947Y - 0.8038Z = -3.9983$
In, 0.020; Cl, 0.001; N(1), −0.010; N(2), −0.010

(c) $0.7279X - 0.3787Y - 0.5716Z = -2.9407^b$
C(11), −0.002; C(12), 0.001; C(13), 0.001; C(14), 0.001;
C(15), 0.002; C(16), 0.002

(d) $-0.9776X + 0.1582Y - 0.1389Z = -3.1048^b$
C(21), −0.008; C(22), 0.003; C(23), 0.007; C(24), −0.011;
C(25), 0.006; C(26), 0.003

[a] Dihedral angles: between planes a and b, 76.0°; between planes c and d, 134°. [b] In atom is 0.080 Å from plane c and 0.281 Å from plane d.

$H_3)_2InCl]_2$, which is described as a distorted octahedron[28] but may perhaps be better viewed as a distorted trigonal bipyramid.

The In–C bond lengths of 2.144 (3) and 2.154 (3) Å compare well with the In–C(aryl) values of 2.111 (14) and 2.155 (14) Å found in $(C_6H_5)_3In$,[13] the sum of the covalent radii being 2.21 Å. Similar values have been observed in alkylindium compounds (2.179 (7) Å in $[(CH_3)_2InCl]_2$,[28] 2.17 Å (average) in $(CH_3)_2InBr$,[29] 2.08 (1) and 2.11 (1) Å in $(CH_3)_2InOAc$,[30] 2.14 Å in $(C_2H_5)_2InOSCH_3$,[31] and 2.16 (2) Å (average) in $[(CH_3)_2In(ON{=}CHC_5H_4N)]_2$[15]). The In–C bond lengths in $[CH_3InCl_2]_2$ (2.052 (9) Å),[16] $(C_2H_5)_2InOAc$ (2.22 and 2.29 Å),[32] and $[In(CH_3)_4]^-$ (2.239 (3), 2.26 (2) Å)[33] fall outside the range of 2.10–2.18 Å derived from the above group of compounds.

There is only a limited amount of information from X-ray studies on In–N bond lengths. In the distorted TBP complex $[(CH_3)_2In(ON{=}CHC_5H_4N)]_2$, the oximate nitrogen atoms form In–N bonds in an equatorial plane of a length (2.271 (16) and 2.288 (15) Å)[15] almost identical with the values for octahedral $[InCl_2(acac)(bpy)]$ (2.276 (4) and 2.299 (4) Å)[27] and very close to those in $InCl_3$·terpy (2.238 (3), 2.268 (3), 2.281 (3) Å).[26] The sum of the covalent radii is 2.19 Å. The present values of 2.442 (3) and 2.482 (2) Å for the two axial In–N bonds in L_2InCl are substantially greater than the "normal" value of ~2.28 Å for an In–N single bond (vide supra) but come close to the only other reported value for axial In–N bonds in a TBP complex, namely, 2.501 (17) and 2.514 (19) Å for the In–N bonds formed by the pyridine nitrogen atoms in $[(CH_3)_2In(ON{=}CHC_5H_4N)]_2$.[15] There are a number of possible reasons for these differences. The apical bonds in TBP complexes are generally weaker than those in the equatorial plane,[20] a diorganoindium chloride will have weaker acceptor properties than $(acac)InCl_2$ or $InCl_3$, and, finally, the skeletal strain in the five-membered chelate rings will contribute to the weakening of the In–N bond (cf. a similar lengthening of the Sn–N bond in $(C_6H_5)_2LSnBr$[21]).

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Supplementary Material Available: A table of observed and calculated structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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Synthesis, Hyperfine Interactions, and Lattice Dynamics of the Intercalation Compounds $FeOCl[(CH_3O)_3P]_{1/6}$ and $FeOCl[(CH_3CH_2)_3P]_{1/6}$

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Trimethyl phosphite (TMP) and triethylphosphine (TEP) have been intercalated into FeOCl to give layer compounds in which half of the "guest" molecule sites in the van der Waals layer are occupied. Intercalation causes a major expansion in the *b*-axis direction of the FeOCl lattice, and room-temperature X-ray powder pattern data show this expansion to correspond to 6.47 and 3.96 Å, respectively. Detailed temperature-dependent ^{57}Fe Mössbauer experiments over the range $4.2 \le T \le 320$ K have shown that there are two different iron atoms in the intercalate corresponding to those Fe atoms which have a "guest" molecule nearest neighbor ($^1/_6$) and those iron atoms which are more distant from the intercalant Lewis base unshared electron pair. The magnetic hyperfine field at liquid-helium temperature is essentially unchanged from that observed in unintercalated FeOCl. The isomer shift and and quadrupole splitting data show a discontinuity at ~220 K, from which it is inferred that the energetics of "guest" molecule binding in the van der Waals layer is on the order of 0.7 kcal mol^{-1}. Fourier-transform infrared spectra of the intercalant show that a number of the fundamental molecular vibrational modes are inhibited when the guest molecule resides in the host lattice and that significant spectral changes in the C–P region occur on sample cooling, again suggesting a direct interaction between the lone-pair electrons of the phosphorus atom and the FeOCl lattice.

Introduction

FeOCl is a layered compound belonging to the orthorhombic space group *Pmnm* (D_{2h}^{13}) with two formula units per unit cell. The crystal structure was initially determined by Goldztaub[2a] and more recently refined by Lind.[2b] The unit cell dimensions are $a = 3.780$, $b = 7.917$, and $c = 3.302$ Å. The crystal structure consists of a stack of double layer sheets of *cis*-

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