The Crystal and Molecular Structure of Dichloro Monothiodibenzoylmethanato Indium Monothiodibenzoylmethane \( \text{InCl}_2 \text{L}(\text{LH}) \)

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X-Ray. Dichloro Monothiodibenzoylmethanato Indium Monothiodibenzoylmethane

Indium trichloride reacts with 2 moles of monothiodibenzoylmethane (LH) in the presence of sodium acetate to yield \( \text{InCl}_2 \text{L}(\text{LH}) \). According to an X-ray structure analysis the molecule possesses a hexacoordinated indium atom with two chlorine atoms in \textit{cis} position and two sulfur atoms in \textit{trans} position. The symmetry of the molecule is \( \text{C}_2 \) imposed by a crystallographic twofold axis. The unique hydrogen atom, assumed to form an intermolecular hydrogen bridge between oxygen atoms could not be detected in the structure analysis.

Introduction

The reaction of monothiodibenzoylmethane \( \text{Ph—C(S)—CH}_2—\text{C(O)—Ph} = \text{LH} \) with anhydrous \( \text{InCl}_3 \) and sodium acetate in ethanol yields \( \text{InL}_3 \) or \( \text{InClL}_2 \), whilst the pyridine adduct \( \text{InCl}_3:3 \text{py} \) produces \( \text{InCl}_2:2 \text{py} \) and \( \text{InClL}_2:2 \text{py} \), respectively. \( \text{InL}_3 \) has been characterized by an X-ray structure analysis [1].

We have now noted that the reaction of \( \text{InCl}_3 \) with 2 moles of LH in the presence of sodium acetate also produces a crystalline compound with composition \( \text{InCl}_2 \text{L}(\text{LH}) \). This provides the first example of a complex where the \( \beta \)-diketone system is attached to the central metal atom in the anionic as well as in the neutral form, both in bidentate fashion.

Experimental

All experimental conditions and methods of analysis were as reported earlier [1]. The molecular weight was determined cryoscopically in benzene. IR spectra were recorded on a Perkin-Elmer-783 spectrometer in the range 4000—200 cm\(^{-1}\) in Nujol mulls and in CH\(_2\)Cl\(_2\) solution. \(^1\)H NMR spectra and \(^{13}\)C NMR data were recorded at 25 °C on a JEOL FX 90 Q NMR spectrometer in CDCl\(_3\) with Me\(_4\)Si as an internal reference.

Dichloro monothiodibenzoylmethanato indium monothiodibenzoylmethane

A solution of monothiodibenzoylmethane (1.7 g, 7.1 mmol) and sodium acetate (0.29 g, 3.5 mmol) in methanol (30 ml) was added dropwise to anhydrous indium trichloride (0.8 g, 3.6 mmol) dissolved in ethanol (15 ml) with continuous stirring at room temperature (32 °C). After the reaction had proceeded for 4 h solvent was removed and the residue extracted with benzene (100 ml). Evaporation of benzene and crystallization of the yellow solid from dichloromethane/n-hexane (1:5) furnished golden yellow crystals of \( \text{InCl}_2 \text{L}(\text{LH}) \), m.p. 209 °C.

\( \text{C}_{36}\text{H}_{23}\text{Cl}_2\text{InO}_5\text{S}_2 \)

<table>
<thead>
<tr>
<th>Calcd</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 54.2 H 3.65 In 17.4 S 9.3</td>
<td>C 54.6 H 3.48 In 17.2 S 9.6</td>
</tr>
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</table>

\( \text{InCl}_2 \text{L}(\text{LH}) \) was monomeric by cryoscopy in benzene (Found M = 660; Calcd M = 665).

X-ray structure determination [2]

The X-ray structure determination was performed using a Syntex P 3 four circle automated diffractometer operating with a graphite monochromator and MoK\(_\alpha\) radiation for data collection and the SHELXTL program package for structure solution and refinement (version 4.1). A NOVA 3 computer from Data General was used in all computational work.

Crystal data

\( \text{C}_{36}\text{H}_{23}\text{Cl}_2\text{InO}_5\text{S}_2, f_w = 664.35, \) monoclinic system, \( a = 21.017(12), b = 8.742(7), c = 19.765(11) \) Å, \( \beta = 128.07(5)°, V = 2859(3) \) Å\(^3\), \( Z = 4, \) space group \( \text{C}2/c, \)

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0340—5087/86/1000—1219$ 01.00/0
Nr. 15 International Tables, \(d_r = 1.543 \text{ g cm}^{-3}\), \(\mu = 10.97 \text{ cm}^{-1}\), single crystal size: \(0.45 \times 0.24 \times 0.3 \text{ mm}\), crystals obtained from methylene chloride/hexane.

**Data collection**

Variable scan speed: 2—29.3°/min for 150—2500 counts/s; scan range 1°; background 0.6°; all data collected for \(h, k, l \pm 2\) in 2\(\theta\) range 2—50°; \(\psi\)-scan for absorption correction; two check reflections measured after every 48 intensity measurements; ambient temperature (25 °C), \(\omega/2\theta\) scan with profile fit. 2793 data collected; 176 of these showed “spikes” or an asymmetric profile and were not used in the calculations. 2617 intensities were converted to structure factors after adjustment of changes in the intensities of the check reflections and application of Lorentz, polarisation and absorption correction (maximum/minimum transmission: 0.943/0.834). 2392 unique \(F_o\); 2126 with \(F_o > 3\sigma(F_o)\) were used in the calculation.

**Structure solution**

Direct methods were applied with the best E-map showing all non hydrogen atoms. These were refined isotropically and anisotropically. The difference Fourier syntheses revealed all hydrogen positions at the carbon atoms. These were included in the final steps of the refinement; only \(U(H22)\) showed a fairly large value (0.12 \(\AA^2\)). One hydrogen atom could not be located. Largest residual peak: 0.038 e/\(\AA^3\). 212 parameters \(p\) were refined; ratio: \(F_o/p = 10.34\). \(R = \sum|\Delta F|/|\Sigma F_o| = 0.0347; R_w = \Sigma w|\Delta F|/|\Sigma \sqrt{w} F_o| = 0.0358\) with \(w = (\sigma(F_o) + 0.00031 (F_o)^2)^{-1}\).

Table I contains the atomic coordinates and \(U_{eq}\) parameters for the nonhydrogen atoms of \(\text{InCl}_2\text{L}(\text{LH})\).

**Results and Discussion**

Indium trichloride reacts with monothiodibenzoylmethane in the presence of sodium acetate as indicated in the equation to yield the golden yellow crystalline dichloromonothiodibenzoylmethanato indium monothiodibenzoylmethane.

\[
\text{InCl}_3 + 2\text{LH} + \text{MeCO}_2\text{Na} \rightarrow \text{InCl}_2\text{L}(\text{LH}) + \text{NaCl} + \text{MeCO}_2\text{H}
\]

The IR spectrum of \(\text{InCl}_2\text{L}(\text{LH})\) shows a single absorption at 1590 cm\(^{-1}\) assignable to \(\nu(C\cdots\cdots\text{O})\) and a band at 1550 cm\(^{-1}\) due to \(\nu(C\cdots\cdots\text{C})\) indicating the chelating nature of the ligands [3, 4] to the indium atom. \(\nu(C\cdots\cdots\text{S})\) can be observed at 1270 and 850 cm\(^{-1}\) (medium), the latter being coupled with \(\text{C-H}\) deformation frequencies [3]. The absence of any band due to uncoordinated \text{CO} and \text{CS} groups excludes the possibility that the \text{LH} ligand is either present as an uncoordinated group or acting as an unidentate monothiodibenzoylmethane ligand. Therefore one has to conclude that the compound shows six-coordination at the indium atom. \(\text{In-Cl, In-O and In-S}\) stretching modes [5] are present in the regions at 310, 440 and 363 cm\(^{-1}\), respectively. \(\text{InCl}_2\text{L}(\text{LH})\) dissolves as a molecular unit in benzene. Careful spectral measurements in solution have not revealed the unique proton of the ligand monothiodibenzoylmethane (LH) either in a terminal (OH, SH) or hydrogen bridging position.

The \(^1\text{H}\) NMR spectrum of \(\text{InCl}_2\text{L}(\text{LH})\) exhibited a multiplet at 7—8.5 ppm due to methine and phenyl protons. It has not been possible to detect the unique hydrogen atom of the ligand LH by this method.

A total of eleven carbon-13 NMR signals are observed for the benzoyl(thiobenzoyl)methanato groups; the \(\delta\) values are \(\text{C(S)}\ 192.8; \text{C(H)}\ 116.0;\ \text{C(O)}\ 181.4;\ \text{i-C}\ 139.0;\ \text{i-C'}\ 146.2;\ \text{o-C}\ 134.0;\ \text{o-C'}\ 131.0;\ \text{m-C}\ 129.4;\ \text{m-C'}\ 128.9;\ \text{p-C}\ 128.7;\ \text{p-C'}\ 127.8 ppm, where \text{i}, \text{o}, \text{m} and \text{p} stand for ipso, ortho, meta and para carbons of the phenyl rings, respectively. Therefore, the spectrum at 25 °C does not
distinguish between the neutral ligand and the deprotonated one, but rather shows that the ligand moieties are chemically equivalent.

In order to try to locate the unique hydrogen in InCl$_2$ L(LH), the X-ray crystal structure was determined. Fig. 1 shows an ORTEP plot of this molecule. Bond lengths and bond angles are summarized in Table II. These allow also a direct comparison with those found for InL$_3$ [1].

The symmetry of the molecule is C$_2$ with a crystallographic two-fold axis passing through the indium atom and bisecting the Cl-In-Cl and O-In-O bond angles. Therefore, pairs of In-Cl, In-S and In-O bonds point to the corners of a distorted octahedron, and the soft ligands (Cl, S) arrange themselves in such a manner that five contacts are established. The alternative coordination, with the oxygen atoms in trans-position would allow only four contacts between the soft atoms.

Although the composition of InCl$_2$ L(LH) requires two different ligand systems L, the C$_2$ symmetry of the molecule makes the ligands chemically and structurally equivalent. In conformity with the IR and NMR data, the unique hydrogen atom could not be located, but it is expected that it acts as an intermolecular bridge (v.i.).

The In-S and In-O bond lengths in InCl$_2$ L(LH) are shorter than in InL$_3$ [1] (2.458(2) Å vs. 2.527(1) Å and 2.128(3) Å vs. 2.208(2) Å). We attribute this to the inductive effect of the chlorine atoms. Also, the In-Cl bond lengths in the complex is shorter than in InCl$_3$ (In-Cl 2.46 Å), which contains a hexacoordinated indium atom [6].

The “bite” of the ligands in InCl$_2$ L(LH) is similar to that found in InL$_3$ as demonstrated by the S-In-O bond angles of 85.8(1)$^\circ$ (83.9—84.2$^\circ$ in InL$_3$), but the trans-bond angles S-In-O(a) (169.3$^\circ$), Cl-In-O(a) (169.9$^\circ$) and Cl(a)-In-O (169.9$^\circ$) deviate by about 6$^\circ$ from the ideal 180$^\circ$ in InL$_3$. This is due to the fact that the two chlorine atoms repel each other, shown by the Cl-In-Cl(a) bond angles of 99.4$^\circ$. All other bonding parameters compare favourably for the two compounds, including the fairly wide In-O-C bond angles (132.4$^\circ$).

The phenyl groups in InCl$_2$ L(LH) are less twisted out of the InOS plane (C(11)-C(15): $\tau$ 11.8$^\circ$; C(21)-C(25): $\tau$ 18.2$^\circ$) than those in InL$_3$. The InSC(l)C(2)C(30) ring shows a boat conformation with C(2) and In sticking out of the plane; however, the boat is very flat, with planes InOS and C(1)C(2)C(3) forming angles of 151.2$^\circ$ and 27.2$^\circ$, respectively, with the OSC(l)C(3) frame.

The packing of the molecules in the crystal lattice is determined by intermolecular H···Cl van der Waals contacts (H(13)···Cl' 3.078 Å, H(21)···Cl' 2.868 Å, H(15)···Cl' 3.429 Å), Cl···S contacts (3.392 Å), O···S contacts (3.139 Å) and Cl···Cl contacts (3.654 Å). More importantly, an O···O contact (transformation 1-x, y, 0.5-z) is present. Its length, 2.76 Å, indicates a perfect distance for hydrogen bonding, and we assume that the unique proton which was not found in the final difference map takes up a position between these two oxygen atoms in the solid state.

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[2] Additional information related to the X-ray structure determination may be obtained from the Fachinformationszentrum Energie, Physik and Mathematik, D-7514 Eggenstein-Leopoldshafen, by quoting the registry number CSD 52100, the authors and the literature citation.