Tris(benzoyl-thiobenzoyl-methanato-O,S)indium, a Conformer of a Facial Isomer

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Tris(benzoyl-thiobenzoyl-methanato-O,S)indium, X-Ray

A second modification of the title compound has been isolated and characterized by an X-ray structure analysis. It crystallizes in the monoclinic space group $P2_1/c$. The indium atom is hexacoordinated and surrounded by three sulfur and three oxygen atoms in a facial arrangement as has been found for a previously known isomer. However, the phenyl groups adopt a different orientation, hence it is a rotamer.

Introduction

The reaction of $InCl_3$ with monothiodibenzoyl-methane (LH) in the presence of sodium acetate (1:3:3) produces a complex InL_3 which has been found by X-ray structure determination to be the facial isomer [1]. A similar reaction performed in a different stoichiometric ratio (1:2:1) gave an unusual *cis*-octahedral complex $InCl_2L \cdot LH$ with two different types of ligands [2]. However, the acidic proton H of the ligand LH could not be located in the X-ray structure analysis. In order to establish the hydrolytic stability of this complex it was treated with aqueous dioxan. Under these conditions a new compound InL_3 is formed whose crystal and molecular structure is described here.

Experimental

All experimental conditions and methods of analysis were those as previously reported [2].

Tris(benzoyl-thiobenzoyl-methanato-O,S)indium (1)

Dichloro(benzoyl-thiobenzoyl-methanato-O,S)-indium-monothiodibenzoyl-methane [2] (0.49 g) was dissolved in 25 ml of dioxan. Adding 15 ml of water resulted in the formation of a yellow precipitate. Its quantity increased on stirring for 30 min. The product (**1**) was filtered, washed with hexane and ethanol and dried for 4 h at 32 °C and 0.1 Torr. Recrystallization from trichloromethane/methanol produced yellow crystals in the form of thin plates. Molecular weight, IR and NMR spectra were found to be almost identical with the InL_3-compound described earlier [1].

X-Ray structure determination of 1

A single crystal (0.1×0.3×0.4 mm) was mounted in a glass capillary, optically centered on the goniometer of an ENRAF-NONIUS CAD4 automated four circle diffractometer, employing graphite monochromatized MoK_α-radiation. The dimensions of the unit cell were determined using the setting angles of 25 automatically centered reflections. — *Crystal data:* $C_{45}H_{33}InO_3S_3$. $M_r = 832.8$, $a = 19.562(3)$, $b = 9.991(2)$, $c = 20.097(4)$ Å, $\beta = 94.17(2)°$, $V = 3917.8(5)$ Å^3, $D_r = 1.41$ g/cm^3, $Z = 4$, space group $P2_1/c$ (Nr. 14), F(000) = 1695, $\mu = 7.84$ cm^{-1}. — *Data collection:* $\omega-2\theta$-scan, scan width $0.80° + 0.349 \tan\theta$, maximum scan time 1.55°/min. 2θ-range: 4–50°, 3 check reflections measured after every 360 intensity measurements, 7527 reflections recorded. — *Data reduction and refinement:* Lorentz, polarization and empirical absorption correction (max./min. transmission: 0.999/0.909). Structure solved by Patterson and subsequent Fourier synthesis. Anisotropic description of nonhydrogen atoms, isotropic refinement of the hydrogen atom coordinates. Final residuals: $R = 0.0336$, $R_w = 0.0349$; 553 parameters refined; largest residual electron density: 0.63 e/Å^3. Final atomic coordinates are summarized in Table I [3]. Calculations were performed on a PDP 11 microcomputer using the program package SDP as supplied by Enraf-Nonius.

Results

The formation of the complex InL_3 (**1**) by treatment of the complex $InCl_2L \cdot LH$ with aqueous dioxan

is not readily explained. It may possibly be formed according to equation (1). No attempt has been

$$3\,InCl_2L \cdot LH \rightarrow 2\,InL_3 + 3\,HCl + InCl_3 \qquad (1)$$
$$\mathbf{1}$$
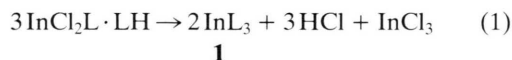
made to isolate the $InCl_3$ expected, which should be present as its dioxan adduct [4]. Since $InCl_2L \cdot LH$ is formed in methanol solution, it may be that the re-distribution of the ligands as described in eq. (1) is primarily due to the better solvation of HCl by water.

1 crystallizes in yellow plates from chloroform/ hexane solution. The crystals proved to be mono-clinic, as were the crystals of complex **2** obtained previously [1] from chloroform/methanol. Even the space groups are identical, namely $P2_1/c$. The cell dimensions differ, however, considerably. The ques-tion, therefore, is, are there two modifications of the same isomer or are there different isomers. As has been pointed out previously, InL_3 may occur as the meridional or the facial isomer **A** or **B,** each as a pair of enantiomers.

A   B
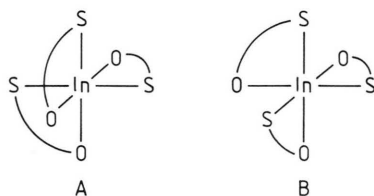
The most important result of the X-ray structure determination is the fact that the complex **1** investi-gated is again the facial isomer of type **2**. Fig. 1 shows a plot of the molecule **1** as well as of **2** approxi-mately in the same orientation. One might, there-fore, conclude that the two specimens investigated are indeed two modifications of the same isomer. However, some bond distances and bond angles de-viate significantly from one another. Data obtained for **1** are summarized in Table II. Thus the InS bond lengths are different in the two species (**1**: 2.523(10), 2.500(3), 2.522(6) Å; **2**: 2.525(2), 2.526(2), 2.530(2) Å) and the same holds for the In−O bond lengths (**1**: 2.182(2), 2.214(3), 2.211(6) Å; **2**: 2.193(3), 2.202(3), 2.221(3) Å). On average the CS bonds (1.713 Å) are a bit shorter in **1** as compared with **2** (1.728 Å) while the InO bonds are of compar-able lengths. Another feature is that there are two wider and one smaller S−In−S angle in **1** (98.9, 98.5 and 91.4°) but two more acute ones in **2** (98.1, 94.2,

Table I. Atomic coordinates (10^4) and equivalent isotropic B-values. Standard deviations in parenthesis.

Atom	x	y	z	B
In	2502.6(1)	1986.5(3)	3592.5(1)	2.923(6)
S 1	3636(6)	2372(1)	3100(1)	4.18(8)
S 2	2927(1)	804(6)	4638(1)	4.10(6)
S 3	2424(1)	4172(1)	4210(6)	4.38(4)
O 1	2057(1)	2664(1)	2624(1)	3.4(3)
O 2	2397(1)	− 22(3)	3131(1)	3.3(1)
O 3	1389(3)	1768(1)	3684(3)	3.2(3)
C 1	3501(1)	2044(3)	2262(1)	3.3(2)
C 2	2894(2)	2064(1)	1871(5)	3.1(1)
C 3	2224(4)	2392(2)	2046(1)	2.9(3)
C 4	2793(2)	−1012(4)	3211(2)	3.1(1)
C 5	3232(5)	−1291(2)	3791(4)	3.4(2)
C 6	3298(4)	− 642(5)	4393(2)	3.2(3)
C 7	937(2)	2656(4)	3645(5)	2.8(1)
C 8	1013(4)	3974(2)	3899(4)	3.2(3)
C 9	1578(1)	4631(4)	4167(2)	3.1(2)
C 10	4136(5)	1710(1)	1931(4)	3.8(3)
C 11	4622(1)	859(5)	2237(1)	4.9(2)
C 12	5196(2)	506(1)	1913(6)	6.2(1)
C 13	5288(5)	1023(2)	1299(1)	6.8(4)
C 14	4828(2)	1876(6)	996(3)	6.7(2)
C 15	4246(5)	2214(2)	1311(6)	5.3(4)
C 20	1651(8)	2389(5)	1516(3)	2.9(3)
C 21	1746(3)	2833(8)	876(5)	3.8(2)
C 22	1201(5)	2917(3)	406(6)	5.0(3)
C 23	559(1)	2530(4)	575(2)	6.0(2)
C 24	467(6)	2062(1)	1199(5)	5.5(3)
C 25	1007(2)	1998(6)	1674(1)	3.9(4)
C 30	2789(3)	−1982(2)	2647(8)	3.0(2)
C 31	2606(5)	−1537(3)	2006(1)	3.9(4)
C 32	2622(2)	−2387(5)	1471(2)	5.0(1)
C 33	2801(5)	−3702(2)	1565(4)	5.3(2)
C 34	2959(4)	−4182(5)	2196(2)	5.1(2)
C 35	2959(2)	−3320(4)	2735(5)	4.1(2)
C 40	3740(6)	−1310(2)	4938(5)	3.6(3)
C 41	3675(2)	−2662(6)	5062(3)	4.5(3)
C 42	4095(6)	−3253(2)	5570(5)	6.0(3)
C 43	4562(1)	−2495(6)	5944(1)	6.9(3)
C 44	4630(2)	−1170(1)	5816(6)	6.4(1)
C 45	4216(5)	− 565(2)	5323(1)	4.8(4)
C 50	247(3)	2261(5)	3344(3)	2.9(1)
C 51	− 173(5)	3189(3)	2998(7)	3.7(5)
C 52	− 802(7)	2799(5)	2700(5)	4.7(3)
C 53	−1014(3)	1504(6)	2751(5)	5.0(2)
C 54	− 608(5)	600(2)	3094(5)	4.9(3)
C 55	46(1)	937(4)	3393(2)	4.0(2)
C 60	1474(5)	5954(1)	4487(4)	3.2(3)
C 61	1597(1)	7134(7)	4170(1)	4.9(3)
C 62	1478(3)	8344(1)	4473(7)	5.8(1)
C 63	1242(6)	8374(3)	5097(2)	5.2(3)
C 64	1119(2)	7210(4)	5413(2)	5.4(1)
C 65	1223(5)	6012(2)	5114(4)	4.7(2)

94.2°). Moreover, the O−In−O bond angles are much more uniform in **2** (79.1, 78.8, 79.0°) than in **1** (83.6, 76.9, 83.3°). In addition, the S_3 plane in **1** is
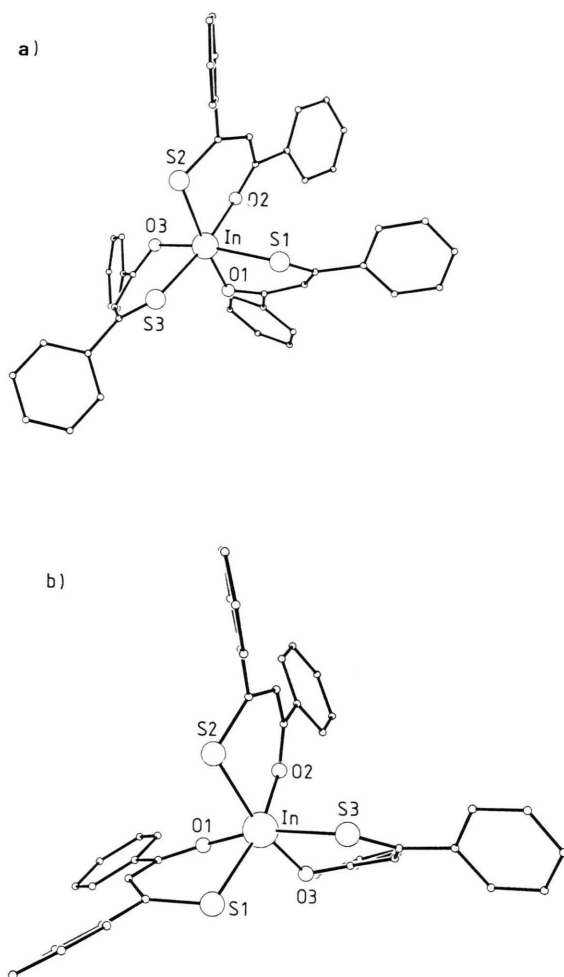
a)

b)

Fig. 1. a) Plot of the molecule 1, hydrogen atoms omitted and numbering restricted to the core atoms; b) plot of the InL$_3$ molecule **2** [1] in approximately the same core orientation as **1**.

tilted by 5.7° towards the O$_3$ plane. The same angle for **2** was found to be only 1.0°. All these features could be accounted for with packing effects. However, the symmetry of the InL$_3$ molecules may still be different inspite of a rather similar InO$_3$S$_3$ core due to different InSC$_3$O ring conformations as well as the orientation of the phenyl rings, e. g. the lattice may stabilize different conformers of the same isomer. Inspection of Fig. 1 shows that the latter is indeed

Table II. Selected bonding parameters for **1**.

Bond length			
In−S1	2.523(10)	In−S2	2.500(3)
In−S3	2.522(6)	In−O1	2.182(2)
In−O2	2.214(3)	In−O3	2.211(6)
S1−C1	1.718(3)	S2−C6	1.706(8)
S3−C9	1.714(2)	O1−C3	1.258(4)
O2−C4	1.259(4)	O3−C7	1.250(6)
C1−C2	1.374(6)	C2−C3	1.421(9)
C4−C5	1.424(9)	C5−C6	1.371(8)
C7−C8	1.416(6)	C8−C9	1.361(9)

Bond angles			
S1−In−S2	98.9(1)	S1−In−S3	98.5(1)
S1−In−O1	84.7(1)	S1−In−O3	161.3(2)
S2−In−S3	91.4(2)	S2−In−O1	169.5(1)
S2−In−O2	86.5(1)	S2−In−O3	98.8(1)
S3−In−O1	97.8(2)	S3−In−O2	169.7(1)
S3−In−O3	87.1(1)	O1−In−O2	83.6(1)
O1−In−O3	76.9(2)	O2−In−O3	83.3(1)
In−S1−C1	106.2(4)	In−S2−C6	106.3(2)
In−S3−C9	107.5(3)	O2−C4−C5	126.0(4)
In−O1−C3	130.0(3)	In−O2−C4	128.4(2)
S2−C6−C5	129.8(5)	In−O3−C7	128.4(3)
O3−C7−C8	125.5(6)	S3−C9−C8	130.0(4)
S1−C1−C2	128.6(5)	O1−C3−C2	125.8(6)
C1−C2−C3	129.4(7)	C4−C5−C6	130.0(6)
C7−C8−C9	130.7(5)		

Table III. Interplanar angles between selected best planes in the InL$_3$ molecule **1**.

	Plane	1	2	3	4	5	6	7	8	9	10
1	S1S2S3	−									
2	O1O2O3	5.7									
3	InS1O1	59.5	55.6								
4	InS2O2	125.5	120.0	87.2							
5	InS3O3	65.4	63.9	99.4	81.2						
6	C10−C15	31.0	28.3	29.5	111.6	86.8					
7	C20−C25	70.3	66.1	11.3	77.2	102.7	40.8				
8	C30−C35	138.1	132.9	99.6	13.9	85.4	125.3	89.0			
9	C40−C45	96.2	90.6	65.5	29.5	67.5	84.3	58.3	43.1		
10	C50−C55	78.9	73.4	59.9	46.6	55.5	71.6	56.1	64.6	17.9	
11	C60−C65	24.3	29.3	83.2	139.6	62.0	53.8	94.2	147.2	113.6	95.7

the case: there are different orientations of the phenyl rings with respect to the S_3 and the O_3 planes. This is most readily recognized by comparing the interplanar angles between the phenyl rings next to S1, S2 and S3 (84.3, 53.8, 113.6° for **1** and 107.5, 73.0 and 57.9° for **2**) or to O1, O2, O3 (89.0, 59,6 and 56,1° for **1** and 86.8, 97.3 and 21.2° for **2,** see also Table III for additional interplanar angles).

This explains also that the NMR data in $CHCl_3$ solution for both species are almost identical. The stabilization of the rotamers of the same InL_3 isomer in the solid state must therefore result from the different conditions of crystallization.

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[2] A. K. Mishra, V. D. Gupta, and H. Nöth, Z. Naturforsch. **41 b,** 1219 (1986).
[3] Additional data related to the X-ray structure determination are deposited at the Fachinformationszentrum Energie, Physik, Mathematik at D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. These may be requested by quoting the number CSD 53313, the authors and the literature citation.
[4] S. H. Whitlow and E. J. Gabe, Acta Crystallogr. **B 31,** 2534 (1975).