Indium Derivatives of Monothio-β-diketones and the *X*-Ray Structure of Tris[benzoyl(thiobenzoyl)methanato-*O,S*]indium(III)†

Channareddy Sreelatha and Vishnu D. Gupta *
Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi, India
Chaitanya K. Narula and Heinrich Nöth *
Institute of Inorganic Chemistry, The University of Munich, Meiserstr. 1, D-8000 München 2, Federal Republic of Germany

---

Six-co-ordinated mono-, bis-, and tris-(monothio-β-diketonates) of indium(III) have been synthesized and characterized. The *X*-ray crystal structure of the title compound reveals a distorted octahedral geometry with facial arrangement of the sulphur and oxygen ligand atoms.

During the past 20 years there has been considerable interest in β-diketonates of metals in main group chemistry with special emphasis on aluminium complexes.[1] Octahedral tris-(β-diketonato)aluminium complexes have been studied extensively, and geometrical and optical isomerism as well as the mechanism of inversion has been established.[2–6] These studies have also been extended to corresponding gallium[7] and indium complexes.[8]

Monothio-β-diketones introduce an additional interesting feature[9–12] because the sulphur atom enhances the acidity of these ligands in comparison to β-diketones, increases their affinity towards 'class b' metals, and also brings about remarkable changes in structural features. So far, reported complexes refer to transition metals,[1,13,14] and the structure of two tris[benzoyl(thiobenzoyl)methanato]iron(III) complexes have been determined.[15] In continuation of our work on main group elements, we report here results on monothio-β-diketonato–indium(III) compounds.

Experimental

All experimental manipulations were carried out under strictly anhydrous conditions. Solvents were purified before use. Monothio-β-diketones[14,16,17] and trichlorotris(pyridine)indium[18] were prepared by reported procedures; indium trichloride (Fluka) was used without further purification.

Indium was estimated as indium oxide and sulphur was analysed by Messenger's method. Molecular masses were determined cryoscopically in benzene. I.r. spectra were recorded on a Perkin-Elmer 621 spectrometer in the range 4 000—200 cm^{-1} in Nujol mulls, and ^{1}H n.m.r. spectra on a Varian EM-360 in $CDCl_3$ ($SiMe_4$ standard). ^{13}C N.m.r. data were recorded with a Bruker WP 200 instrument.

General Procedure for the Preparation of Derivatives (**2**)—(**5**).—A solution of the monothio-β-diketone and sodium acetate in methanol was added dropwise to anhydrous indium trichloride dissolved in methanol (*ca.* 20 cm^3) with continuous stirring at ambient temperature. After complete addition stirring was continued for 3—4 h and a precipitate formed. Volatiles were removed and the residue was extracted with benzene. Removal of solvent and crystallization from chloroform–methanol (1:3) furnished yellow crystalline materials.

The pyridine adducts were similarly synthesized from trichlorotris(pyridine)indium. Results are summarized in Table 1.

X-*Ray Analysis of* (**3a**).—*Crystal data.* $C_{45}H_{33}InO_3S_3$, M = 832.77, monoclinic, space group $P2_1/c$ (no. 14), a = 12.280(4), b = 18.261(6), c = 17.484(4) Å, β = 90.95(2)°, U = 3 920.6(6) Å^3, Z = 4, D_c = 1.41 g cm^{-3}, F(000) = 1 695.98, μ(Mo-K_α) = 7.53 cm^{-1}.

Golden yellow acicular single crystals with rhombohedral habitus were obtained from benzene–hexane solution. A specimen of approximate dimensions 0.23 × 0.15 × 0.4 mm was selected and mounted in a glass capillary. It was optically aligned on the goniometer of a Syntex P3 automated four-circle diffractometer, and the setting angles of 25 automatically centred reflections were used to determine the orientation matrix and the dimensions of the unit cell. The latter were checked by axial photographs. Graphite monochromated Mo-K_α radiation was used (λ = 0.710 69 Å).

The intensities of 6 908 independent reflections in the θ range 1—25° were measured; two check reflections were recorded after every 48 intensity measurements. The measured intensities were corrected for any change in the intensities of the check reflections. Lorentz and polarisation corrections were applied also, and an empirical absorption correction. Intensities were converted to structure factors by standard procedures; 5 576 reflections had $I > 3\sigma(I)$.

A sharpened Patterson map was used to determine the position of the In atom, and all non-hydrogen atoms were then found in a Fourier map. Refinement with individual isotropic temperature factors with rigid phenyl groups converged to R = 0.081. The positions of the phenyl hydrogen atoms were calculated and refined isotropically. At that stage the three remaining hydrogen atoms of the methine groups were located. Final refinement with anisotropic temperature factors for all non-hydrogen atoms and isotropic temperature factors for all hydrogen atoms led to the final R = 0.0442 and R' = 0.0412 [$R = \Sigma|\Delta F|/\Sigma|F_o|$ and $R' = \Sigma(|\Delta F|\sqrt{w})/\Sigma(\sqrt{w}|F_o|)$. The weighting scheme applied was $w = [\sigma^2(F_o) + 0.0003(F_o)^2]^{-1}$. 569 Parameters were refined in the last cycles using blocked cascade calculations. All computations were executed on a NOVA 3 using the SHELXTL programs.[19] Final atomic co-ordinates are given in Table 2.

Results and Discussion

Since Group 3 elements are 'class a' metals, a decreased affinity of monothio-β-diketones (**1**) was expected towards them. However, aluminium derivatives[20] can be prepared conveniently by the reaction of aluminium alkoxides with monothio-β-diketones. The poor solubility of these compounds prevented any characterization; tris(monothioacetylacetonato)-aluminium was totally insoluble in many organic solvents. We

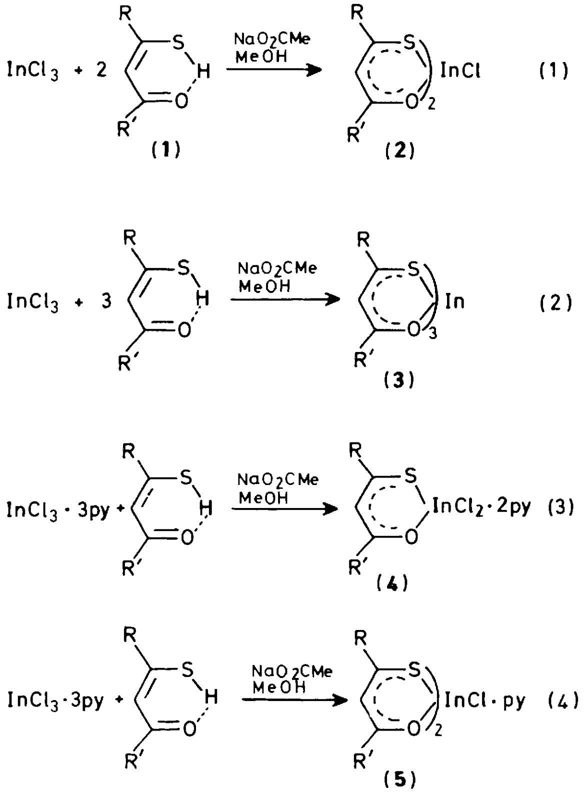
---

† *Supplementary data available* (No. SUP 56326, 5 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Monothio-β-diketonates of indium(III)

Complex	Reactants			Molar ratio	Product formula	M.p. (°C)	Analysis[a] (%)		M[a]
		RCSCH$_2$COR′ (HL)							
		R	R′				In	S	
(3a)	InCl$_3$	Ph	Ph	1:3	InL$_3$	177—180	14.75 (13.80)	11.85 (11.60)	902 (831)
(3b)	InCl$_3$	Ph	–C$_6$H$_4$Me	1:3	InL$_3$	—	12.60 (13.15)	10.85 (11.00)	793 (873)
(3c)	InCl$_3$	Ph	–C$_6$H$_4$Br	1:3	InL$_3$	182	11.15 (10.75)	9.05 (9.00)	—
(3d)	InCl$_3$	Me	Ph	1:3	InL$_3$	145—148	18.80 (17.75)	15.65 (14.85)	631 (645)
(2a)	InCl$_3$	Ph	Ph	1:2	InL$_2$Cl	110—112	18.65 (18.25)	10.25 (10.20)	1 379 (1 256)
(4a)	InCl$_3$·3py	Ph	Ph	1:1	In(L)Cl$_2$·2py	150—155	18.15 (19.85)	5.35 (5.55)	625 (578)
(4b)	InCl$_3$·3py	Ph	–C$_6$H$_4$Me	1:1	In(L)Cl$_2$·2py	185[b]	18.05 (19.35)	5.50 (5.40)	603 (593)
(4c)	InCl$_3$·3py	Ph	–C$_6$H$_4$Br	1:1	In(L)Cl$_2$·2py	169[b]	17.15 (17.45)	4.55 (4.85)	619 (657)
(5a)	InCl$_3$·3py	Ph	Ph	1:2	InL$_2$Cl·py	182	16.15 (16.25)	8.90 (9.05)	732 (707)
(5b)	InCl$_3$·3py	Ph	–C$_6$H$_4$Me	1:2	InL$_2$Cl·py	135[b]	15.60 (15.60)	8.85 (8.70)	819 (735)
(5c)	InCl$_3$·3py	Ph	–C$_6$H$_4$Br	1:2	InL$_2$Cl·py	155	13.45 (13.30)	7.80 (7.90)	839 (863)

[a] Calculated values are given in parentheses. [b] With decomposition.



	a	b	c	d
R	Ph	Ph	Ph	Me
R′	Ph	C$_6$H$_4$Me-*p*	C$_6$H$_4$Br-*p*	Ph

Scheme.

have found that indium complexes of (**1**) are more soluble than the aluminium analogues in common organic solvents.

Indium trichloride reacts with monothio-β-diketones to yield the bis- and tris-(monothio-β-diketonato)indium(III) compounds (**2a**) and (**3a**)—(**3d**) respectively (Scheme).

A monoligand complex InCl$_2$L which would exhibit four-co-ordination at indium could not be obtained. However, trichlorotris(pyridine)indium reacts with monothio-β-diketones to give the products (**4a**)—(**4c**) and (**5a**)—(**5c**) according to equations (3) and (4) (Scheme). All these complexes contain six-co-ordinated indium atoms. This can be deduced from the composition of the compounds of types (**3**)—(**5**), which are monomeric in solution, and from the dimerization of (**2**) in connection with i.r. and n.m.r. data. Compounds of types (**3**), (**4**), and (**5**) are monomeric in benzene solution whereas (**2**) achieves six-co-ordination by dimerization.

A decrease in ν(C⋯O) and ν(C⋯C), to 1 580—1 560 and 1 550—1 530 cm^{-1} respectively, compared with free monothio-β-diketones indicates the chelating nature of the ligand.[1,13,14,16] ν(C⋯S) can be observed at 1 270—1 225 (strong) and 840 ± 5 cm^{-1} (medium to weak), the latter being coupled with C–H deformation frequencies. No bands for unco-ordinated CO and CS groups are observed. This excludes unidentate monothio-β-diketone ligands in these compounds, and substantiates six-co-ordination at the indium atoms. In–Cl, In–O, and In–S stretching modes[21] are present in the regions 300—324, 405—432, and 365—390 cm^{-1} respectively; no In–Cl band at 300 cm^{-1} was found for (**2**) indicating the absence of a terminal In–Cl bond, suggesting bridging Cl atoms to achieve dimerization. Characteristic bands at 690, 753, 1 034, 1 059, and 1 600 cm^{-1} for co-ordinated pyridine in (**4**) and (**5**) have also been observed.

The ^{1}H n.m.r. spectra of compounds (**2**)—(**5**) offered no information on detailed structural features of these compounds. However, ^{13}C n.m.r. allowed the distinction between several alternatives. Dynamic behaviour can be excluded at least for compound (**3a**), since its n.m.r. spectrum was virtually temperature independent. Solubility problems prohibited studies at temperatures lower than −40 °C. Table 3 lists data obtained in CDCl$_3$ solution. Carbon-13 chemical shifts for compounds (**2a**), (**3a**), and (**5a**) are given in Table 3; SiMe$_4$ is used as standard. The spectra were obtained with a Bruker WP 200 n.m.r. spectrometer with proton decoupling.

A total of 11 carbon-13 n.m.r. signals are expected for a benzoyl(thiobenzoyl)methanato-group. For tris[benzoyl(thiobenzoyl)methanato-*O*,*S*]indium, (**3a**), only ten signals were recorded. From these the signal at 128.5 p.p.m. was fairly broad and of higher intensity than the rest. We assume that this signal represents two ^{13}C atoms which are accidentally degenerate. The fact that only 10 signals are observed indicates fairly high symmetry, and this rules out the two enantiomers (**I**) and (**II**). (**III**) and (**IV**) may have C_3 symmetry, and this would be in accord with the n.m.r. result, assuming free rotation of the phenyl groups.

Eleven ^{13}C n.m.r. signals are observed for the chloro-

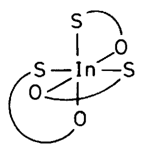
Table 2. Final atomic co-ordinates (× 10^4)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
In	1 473(1)	1 154(1)	2 361(1)	C(25)	−721(4)	2 142(3)	5 011(3)
S(1)	1 913(1)	331(1)	1 247(1)	C(26)	−159(3)	2 288(2)	4 344(2)
S(2)	1 452(1)	121(1)	3 323(1)	C(31)	2 822(4)	−405(3)	4 733(3)
S(3)	3 424(1)	3 421(1)	2 575(1)	C(32)	3 201(5)	−864(3)	5 310(4)
O(1)	−207(2)	1 088(1)	1 924(2)	C(33)	2 664(5)	−916(3)	5 990(3)
O(2)	602(2)	1 772(1)	3 258(1)	C(34)	1 748(4)	−509(3)	6 106(3)
O(3)	1 288(2)	2 231(1)	1 808(1)	C(35)	1 367(4)	−45(2)	5 538(2)
C(1)	777(3)	−222(2)	1 106(2)	C(36)	1 899(4)	14(2)	4 842(2)
C(2)	−280(3)	−65(2)	1 282(2)	C(41)	5 265(3)	2 524(2)	3 268(2)
C(3)	−734(3)	600(2)	1 575(2)	C(42)	6 304(4)	2 804(3)	3 398(3)
C(4)	1 476(3)	512(2)	4 223(2)	C(43)	6 705(4)	3 346(3)	2 933(3)
C(5)	1 071(3)	1 180(2)	4 436(2)	C(44)	6 073(4)	3 618(3)	2 346(3)
C(6)	573(3)	1 724(2)	3 972(2)	C(45)	5 027(3)	3 346(2)	2 215(3)
C(7)	3 499(3)	2 496(2)	2 499(2)	C(46)	4 614(3)	2 797(2)	2 674(2)
C(8)	2 696(3)	2 985(2)	2 309(2)	C(51)	−2 545(3)	367(2)	905(3)
C(9)	1 613(3)	2 850(2)	2 041(2)	C(52)	−3 627(3)	548(3)	776(3)
C(11)	1 966(3)	−1 307(2)	809(2)	C(53)	−4 085(4)	1 101(3)	1 194(3)
C(12)	2 130(4)	−1 974(3)	452(3)	C(54)	−3 476(4)	1 486(4)	1 724(3)
C(13)	1 363(4)	−2 269(3)	−21(3)	C(55)	−2 408(4)	1 315(3)	1 846(3)
C(14)	388(4)	−1 902(2)	−147(2)	C(56)	−1 920(3)	748(2)	1 445(2)
C(15)	211(3)	−1 242(2)	213(2)	C(61)	1 013(4)	4 147(2)	2 336(3)
C(16)	989(3)	−930(2)	704(2)	C(62)	203(4)	4 676(3)	2 342(4)
C(21)	−287(4)	2 966(2)	3 995(2)	C(63)	−794(4)	4 529(3)	2 035(4)
C(22)	−960(4)	3 485(3)	4 305(3)	C(64)	−999(4)	3 860(4)	1 716(4)
C(23)	−1 521(4)	3 340(3)	4 954(3)	C(65)	−216(4)	3 326(3)	1 715(3)
C(24)	−1 403(4)	2 675(3)	5 305(3)	C(66)	805(3)	3 464(2)	2 009(2)

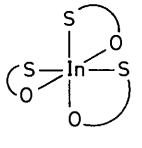
Table 3. Carbon-13 n.m.r. chemical shifts

	C^1	C^2	C^3	*i*-C	*i*-C′	*o*-C	*o*-C′	*m*-C	*m*-C′	*p*-C	*p*-C′
(3a)	191.5	116.1	186.2	139.7	147.0	128.2	127.6	128.5	128.5	130.0	132.7
(2a)	191.3	114.8	184.6	137.5	143.8	129.0	128.1	129.2	128.9	134.6	132.0
(5a)*	191.6	115.4	180.0	137.8	135.4	127.9	126.8	128.8	128.6	134.3	131.3
	191.3	110.7	178.0	136.5	135.3	128.5	127.3	128.9	128.7	132.6	131.1

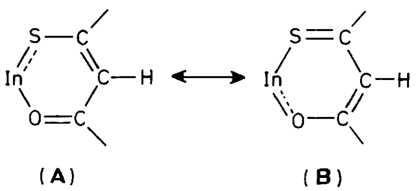
* Signals from co-ordinated pyridine at 135.9, 130.1, and 129.2 p.p.m.



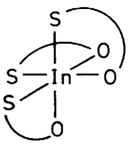
(I)



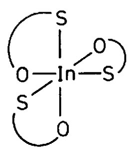
(II)



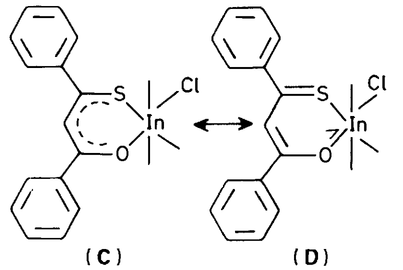
(A) (B)



(III)



(IV)



(C) (D)

compound (**2a**). Assuming chloride bridges for the six-co-ordinated indium, structures (**V**) and (**VI**) would be acceptable. From these we favour (**V**) because the C^3 and C^2 atoms are better shielded than in compound (**1**) indicating a substantial contribution of resonance form (**D**) to the ground state. This is in accord with a better shielded *ipso*-carbon atom for the phenyl group bonded to the carbonyl moiety. Assignment of the signal at 184.6 p.p.m. to C^3 rests on the fact that it is broader than that at 191 p.p.m., due to the proximity to oxygen. The methine carbon atom is easily recognised and can be assigned unambiguously. This is also true for the *ipso*- and *para*-carbon atoms of the phenyl rings. For isomer (**V**) we would expect a less significant influence of the Cl atoms on the shielding of carbon atom C^3. Moreover, we know from the *X*-ray structure of (**3a**) that 'soft' atoms tend to be next to each other in the co-ordination sphere of indium, and this finding tends to favour structure (**V**).

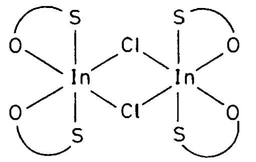
Table 4. Bond lengths (Å) and angles (°) with standard deviations in parentheses

(a) Bond lengths

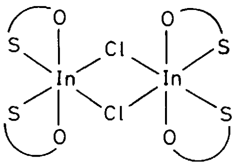
In–S(1)	2.525(2)	C(5)–C(6)	1.435(5)	C(1)–C(16)	1.496(5)	S(3)–C(7)	1.718(4)
In–O(1)	2.193(3)	C(7)–C(46)	1.502(5)	C(4)–C(5)	1.371(5)	O(3)–C(9)	1.264(4)
S(1)–C(1)	1.737(4)	In–S(2)	2.526(2)	C(6)–C(26)	1.494(5)	C(2)–C(3)	1.435(5)
O(1)–C(3)	1.254(5)	In–O(6)	2.221(3)	C(8)–C(9)	1.425(5)	C(4)–C(36)	1.499(6)
C(1)–C(2)	1.370(5)	S(2)–C(4)	1.728(4)	In–S(3)	2.530(2)	C(7)–C(8)	1.367(5)
C(3)–C(56)	1.496(5)	O(2)–C(6)	1.254(5)	In–O(3)	2.202(3)	C(9)–C(66)	1.499(5)

(*b*) Bond angles

S(1)–In–S(2)	94.2(0)	C(4)–C(5)–C(6)	128.8(4)	C(6)–O(2)–In	135.0(2)	S(3)–In–O(3)	83.9(1)
S(1)–In–O(1)	84.9(1)	C(5)–C(6)–C(26)	119.4(3)	S(1)–C(1)–C(16)	115.1(3)	O(2)–In–O(3)	79.0(1)
S(2)–In–O(1)	99.8(1)	C(7)–C(8)–C(9)	129.2(4)	O(1)–C(3)–C(2)	125.1(3)	C(7)–S(3)–In	109.4(1)
S(3)–In–O(1)	162.1(1)	C(8)–C(9)–C(66)	119.8(3)	S(2)–C(4)–C(36)	114.0(3)	C(9)–O(3)–In	128.9(2)
O(1)–In–O(2)	79.1(1)	S(2)–In–S(3)	98.1(0)	O(2)–C(6)–C(5)	125.0(3)	C(2)–C(1)–C(16)	117.3(3)
C(1)–S(1)–In	105.9(1)	S(1)–In–O(2)	163.4(1)	S(3)–C(7)–C(8)	129.0(3)	O(1)–C(3)–C(56)	116.0(3)
C(3)–O(1)–In	133.1(2)	S(2)–In–O(2)	84.2(1)	O(3)–C(9)–C(8)	123.3(3)	C(5)–C(4)–C(36)	117.8(3)
C(2)–C(1)–S(1)	127.5(3)	S(3)–In–O(2)	102.3(1)	S(1)–In–S(3)	94.2(0)	O(2)–C(6)–C(26)	115.6(3)
C(1)–C(2)–C(3)	129.3(3)	O(1)–In–O(3)	78.8(1)	S(1)–In–O(3)	102.4(1)	C(8)–C(7)–C(46)	117.5(3)
S(2)–C(4)–C(5)	127.9(3)	C(4)–S(2)–In	107.3(1)	S(2)–In–O(3)	163.1(1)	O(3)–C(9)–C(66)	116.9(3)



(V)



(VI)

The ^{13}C n.m.r. spectrum of (**5a**) shows two sets of eleven signals plus signals attributable to co-ordinated pyridine. Therefore the compound must be less symmetric than the two previous ones. Two isomers are to be expected with Cl and py *trans* to each other having point group symmetry C_i or C_s respectively (assuming freely rotating phenyl groups). These isomers can be ruled out, because they should bring about only 11 ^{13}C resonances for the benzoyl(thiobenzoyl)methanato-ligand. Therefore, (**5a**) should be a *cis* complex, and four pairs of enantiomers do exist for this situation. Carbon-13 n.m.r. will not allow distinction between these isomers. Assignments in Table 3 for compound (**5a**) are strictly tentative. Since *ipso-* and *para-*C atoms of the phenyl rings are better shielded as is the carbon atom C^3, we correlate the better shielded C atoms in (**5a**) with the better shielded C^3 of one of the ligands and, consequently, the deshielding of *ortho-* and *meta-*carbon atoms. However, the differences are rather small, and it is very difficult to make an unambiguous assignment. In addition, ^{13}C n.m.r. clearly indicates the presence of small amounts of a second isomer in the sample; data for this have not been included in Table 3. However, the ^{13}C n.m.r. spectrum will not allow distinction between the four isomers.

The solution of the isomer problem for (**5a**) must await an *X*-ray structure determination. Although the n.m.r. results for (**2a**) favour a structure with a facial arrangement of the oxygen and sulphur atoms in a pseudo-octahedral environment, proof must also come from an *X*-ray determination of its structure.

X-Ray Structure of Tris[benzoyl(thiobenzoyl)methanato]indium.—Since monothio-β-diketones act as bidentate ligands the isomers (**I**)—(**IV**) may be expected to assume a pseudo-octahedral environment at the indium atom. Isomers (**I**) and (**II**) possess a meridional arrangement of sulphur and oxygen atoms while the co-ordination in the two optical isomers (**III**) and (**IV**) shows a facial arrangement of these atoms. The overall symmetry of these isomers is low, at best C_3 for (**III**) and (**IV**) and C_1 for (**I**) and (**II**).

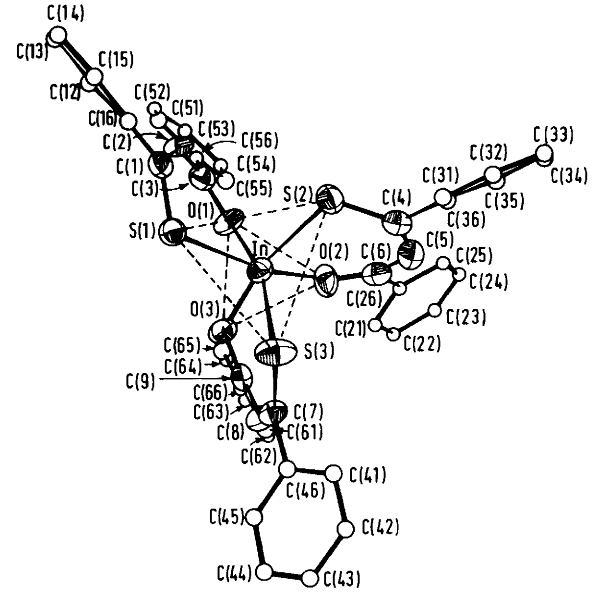


Figure. ORTEP plot of tris[benzoyl(thiobenzoyl)methanato]indium. Thermal ellipsoids represent a 50% probability level

The results of the *X*-ray structure determination of (**3a**) show that it possesses a facial 'octahedral' geometry as demonstrated in the Figure.

As is evident from the data in Table 4 all In–S bonds are equal. This bond is 0.14 Å shorter than the sum of the covalent radii of the atoms. In contrast, the In–O bonds appear not to be equal as judged by their standard deviations; however, differences are small, the average being 2.205 Å. The three oxygen atoms form an almost perfect equilateral triangle in contrast to the three sulphur atoms, where only two edges are of equal lengths [S(1) ··· S(2), 3.701, S(3) ··· S(1) 3.704 Å] while the third is somewhat longer [S(2) ··· S(3) 3.819 Å]. Consequently, the S–In–S bond angles differ much more (up to 3.9°) than the O–In–O bond angles (0.3°). The most significant distortion in the octahedral angles is found for S(2)–In–O(1) (99.8°); the In–O–C bond angles show that the ligands, in the

Table 5. Interplaner angles (°) between the best planes defined by the atoms listed

No.	Atoms	1	2	3	4	5	6	7	8	9	10	11	12	13
1	S(1)—S(3)													
2	O(1)—O(3)	1.0												
3	In,O(1),S(1)	116.3	115.5											
4	In,O(2),S(2)	62.5	62.4	79.7										
5	In,O(3),S(3)	114.3	115.0	102.8	76.5									
6	In,S(1),C(1),C(2),C(3),O(1)	116.4	115.5	18.5	95.3	116.4								
7	In,S(2),C(4),C(5),C(6),O(2)	63.6	63.2	67.3	15.3	89.4	81.2							
8	In,S(3),C(7),C(8),C(9),O(3)	107.3	108.1	117.7	83.7	15.3	130.0	98.3						
9	C(11)—C(16)	93.4	92.5	26.2	77.9	126.5	24.1	62.3	141.8					
10	C(21)—C(26)	69.2	69.3	84.2	11.9	64.6	101.4	26.8	71.9	86.8				
11	C(31)—C(36)	93.2	93.0	61.7	30.7	61.2	80.2	33.7	74.1	73.0	26.8			
12	C(41)—C(46)	134.9	135.5	81.9	83.0	23.5	93.6	91.2	36.5	107.5	72.6	57.9		
13	C(51)—C(56)	105.6	104.7	13.2	79.9	115.4	15.8	65.5	130.5	13.2	86.8	68.1	95.0	
14	C(61)—C(66)	92.2	91.3	34.0	87.6	136.6	24.6	71.8	151.7	11.7	97.3	84.7	115.7	21.2

solid state, are non-equivalent, because the largest difference in this bond angle is 6.1°. All C atoms of the benzoyl(thiobenzoyl)-methanato-unit are of sp^2 type as is evident by the sum of the bond angles. Interestingly, the C–C–C angles to the central methine unit have widened to *ca.* 129°.

There are greater differences in S–C bond distances than in the C–O distances. Comparable C–C bonds are all equal, and a typical alternation is found in the ligand framework suggesting that the negative charge on the ligand resides preferably on sulphur, *e.g.* resonance form (**A**) contributes more significantly to the structure than (**B**).

The overall symmetry of the complex is C_1; there is no symmetry element due to the unequal conformation of the non-planar six-membered chelate rings and to the arrangement of the phenyl rings. This low symmetry is also found for the first co-ordination sphere at the indium atom as evidenced by the interplanar angles of planes 5, 6, and 7 (see Table 5) to planes 1 and 2 or amongst themselves.

The planes S(1)—S(3) and O(1)—O(3) (1 and 2 respectively) are nearly parallel, and they are separated from one another by 2.81 Å with the indium atom being 1.31 Å from plane 1 and 1.5 Å from plane 2. Also, the intraligand O–In–S planes are different, forming interplanar angles to plane 1 of 116.3, 114.3, and 62.5°.

All chelate rings have the common feature that the indium atom sticks out from the best plane through the rest of the ring atoms, which do not deviate grossly from this plane.

The phenyl rings next to sulphur form interplanar angles with plane 1 of 93.4, 93.2, and 134.9°; those next to plane 2 form angles of 105.6, 69.2, and 92.2°. Only one of the phenyl groups is almost coplanar with the best plane of its chelate ring, namely C(51)—C(56); all others are twisted by 24—36°, and it is important to note that the phenyl ring C(61)—C(66) is twisted in a different direction than all other phenyl groups.

Althought (**3a**) has a structure similar to the corresponding iron(III) complex,[15] structural details are different. Thus, the mean In–S bond is 0.15 Å longer than the mean Fe–S bond, while the In–O bond exceeds the Fe–O bond by 21 pm. This may indicate a stronger interaction between the soft acid In^{3+} (as compared with Fe^{3+}) to the soft sulphur ligands. On the other hand, the In–S distance in (**3a**) corresponds closely to the bond length found in tris(dialkyldithiocarbamato)indium (2.852 Å)[22,23] or diethyl(monothioacetato)indium (2.632 Å).[24] In contrast, the In–S bonds in In_2S_3,[25] which contains six-co-ordinated indium atoms, are substantially shorter (2.51—2.54 Å). However, these bond lengths cannot directly be compared with those of the co-ordination compounds because the co-ordination at the sulphur atom is different. A comparison of the In–O bond lengths in (**3a**) (average 2.205 Å) with those found in tris(acetylacetonato)indium (average 2.128 Å),[26] tris(pentane-2,4-dionato)indium (average 2.132 Å),[27] and *cis*-(acetylacetonato)(2,2′-bipyridyl)dichloroindium (2.124, 2.164 Å)[28] shows longer bonds in (**3a**). This supports the conclusion drawn from the differences between the M–S and M–O bonds (M = Fe or In) for (**3a**) and its iron analogue.

Acknowledgements

Dr. C. K. Narula and Miss Ch. Sreelatha are grateful respectively to Humboldt-Stiftung (Federal Republic of Germany) and to the Council of Scientific and Industrial Research (India) for awards.

References

1 R. C. Mehrotra, R. Bohra, and D. P. Gaur, 'Metal-β-diketonates and Allied Derivatives,' Academic Press, London, 1978.
2 A. Werner, *Ber. Dtsch. Chem. Ges.*, 1921, **45**, 3061.
3 J. C. Bailar, jun. *J. Inorg. Nucl. Chem.*, 1958, **8**, 165.
4 C. S. Springer, jun., and R. E. Sievers, *Inorg. Chem.*, 1967, **6**, 852.
5 B. Jurado and C. S. Springer, jun., *Chem. Commun.*, 1971, 85.
6 R. C. Fay and T. S. Piper, *J. Am. Chem. Soc.*, 1963, **85**, 500.
7 P. J. Pinnavaia, J. M. Sebesen II, and D. A. Case, *Inorg. Chem.*, 1969, **8**, 604.
8 R. C. Fay and T. S. Piper, *J. Am. Chem. Soc.*, 1962, **84**, 2303.
9 S. K. Saini, V. D. Gupta, and R. C. Mehrotra, *J. Indian Chem. Soc.*, 1982, **59**, 1424.
10 S. K. Saini, V. D. Gupta, and R. C. Mehrotra, *Aust. J. Chem.*, 1982, **35**, 2215.
11 S. K. Saini, V. D. Gupta, R. C. Mehrotra, and R. P. Tripathi, *Aust. J. Chem.*, 1980, **33**, 1137.
12 R. K. Kanjolia and V. D. Gupta, *Inorg. Nucl. Chem. Lett.*, 1980, **16**, 449.
13 S. E. Livingstone, *Coord. Chem. Rev.*, 1971, **7**, 59.
14 M. Cox and J. Darken, *Coord. Chem. Rev.*, 1971, **7**, 21.
15 B. F. Hoskins and C. D. Paunan, *Inorg. Nucl. Chem. Lett.*, 1975, **11**, 409.
16 L. Carlsen and F. Duns, *Synthesis*, 1977, 256.
17 E. Uhlemann and P. Thomas, *J. Prakt. Chem.*, 1966, **34**, 180.
18 B. F. G. Johnson and R. A. Walton, *Inorg. Chem.*, 1966, **5**, 49.
19 G. M. Sheldrick, SHELXTL, program for crystal structure determination, Göttingen, 1983.
20 R. K. Kanjolia, C. K. Narula, and V. D. Gupta, *Curr. Sci.*, 1982, **51**, 983.
21 D. M. Adams, A. J. Carty, P. Carty, and D. G. Tuck, *J. Chem. Soc. A*, 1968, 162; J. G. Contreras and D. G. Tuck, *J. Chem. Soc., Dalton Trans.*, 1974, 1249.
22 H. D. Hausen and H. J. Guder, *J. Organomet. Chem.*, 1974, **57**, 243.

23 P. J. Hauser, J. Bordner, and A. F. Schreiner, *Inorg. Chem.*, 1973, **12**, 1347.
24 H. D. Hausen, Proceedings of European Crystallographic Meeting, 1974, vol. 2, p. 310.
25 R. Diehl and C. D. Carpenter, *Acta Crystallogr., Sect. B*, 1977, **32**, 1257; K. J. Range, *Z. Naturforsch, Teil B*, 1978, **33**, 463.
26 J. G. Rodriguez, F. F. Cano, and S. Garcia-Blanco, *Cryst. Struct. Commun.*, 1979, **8**, 53.
27 G. J. Palenik and K. R. Dymock, *Acta Crystallogr., Sect. B*, 1980, **36**, 2059.
28 J. G. Contreras, F. W. B. Einstein, and D. G. Tuck, *Can. J. Chem.*, 1974, **52**, 3793.

Received 19th October 1984; *Paper* 4/1789