Pergamon

PII: S0277–5387(96)00536–0

Polyhedron Vol. 16, No. 13, pp. 2291–2298, 1997
© 1997 Elsevier Science Ltd
All rights reserved. Printed in Great Britain
0277–5387/97 $17.00+0.00

Mixed-ligand complexes of indium(III). Reactions of $[InCl_3(L^1)(MeOH)]$ with bidentate ligands. Synthesis, characterization and X-ray structures of $[In(L^1)Cl(ox)(OH_2)]\cdot 2H_2O$, $[In(L^1)Cl(mnt)]\cdot MeOH$ and $[In(pythio)_3]$ [L^1 = pyridine-2,6-bis(acetyloxime), ox^{2-} = oxalate, mnt^{2-} = 1,2-dicyanoethene-1,2-dithiolate, $pythio^-$ = pyridine-2-thiolate]

Sonja Abram,* Cäcilia Maichle-Mössmer and Ulrich Abram

Institute of Inorganic Chemistry, University of Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany

(Received 26 September 1996; accepted 25 October 1996)

Abstract—$[InCl_3(L^1)(MeOH)]$ [L^1 = pyridine-2,6-bis(acetyloxime), $2,6\text{-}C_5H_3N(C_2H_3NOH)_2$] reacts with bidentate ligands by ligand exchange. A seven-coordinate complex of the composition $[In(L^1)Cl(ox)(OH_2)]$ is formed with potassium oxalate (K_2ox). The oxalato ligand occupies the equatorial plane of a pentagonal bipyramid together with the tridentate amine oxime. With sodium 1,2-dicyanoethene-1,2-dithiolate (Na_2mnt) the analogous reaction produces a six-coordinate mixed ligand complex, $[In(L^1)Cl(mnt)]$, which has a distorted octahedral coordination sphere. Ligands which form four-membered chelate rings like dialkyldithiocarbamates, R_2dtc^-, or pyridine-2-thiolate, $pythio^-$, are able to replace all ligands of $[InCl_3(L^1)(MeOH)]$ to form neutral tris chelates. The structure of $[In(pythio)_3]$ has been elucidated showing a strong distortion of the coordination polyhedron from the idealized octahedral geometry. © 1997 Elsevier Science Ltd

Keywords: indium; mixed-ligand complexes; nitrogen donor ligands; X-ray structures.

There are only a few examples of indium complexes with oxime ligands. An organometallic indium(III) compound which contains two $InMe_2$ units bridged by two pyridine-2-carbaldehyde oximato ligands [1] has been structurally characterized. Deprotonation enables the ligand to become tridentate and to bridge the two metal centres.

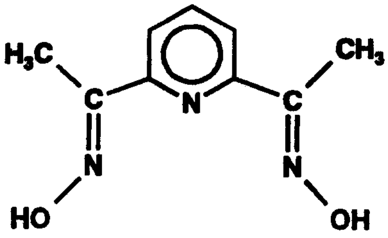
We reported syntheses and structures of indium(III) complexes with pyridine-2,6-bis(acetyloxime) L^1 (**I**), which acts as tridentate chelator and reacts with $InCl_3$ in methanol to give the seven-coordinate complex $[InCl_3(L^1)(MeOH)]$ (**II**). In this complex, the tridentate amine oxime occupies the equatorial plane of a pentagonal bipyramide together with Cl^- and CH_3OH [2]. In the present paper, we describe reactions of **II** with bidentate ligands and the molecular structures of the reaction products with potassium oxalate, K_2ox (**III**), sodium 1,2-dicyanoethene-1,2-dithiolate, Na_2mnt (**IV**), and pyridine-2-thiol, Hpythio (**V**).

EXPERIMENTAL

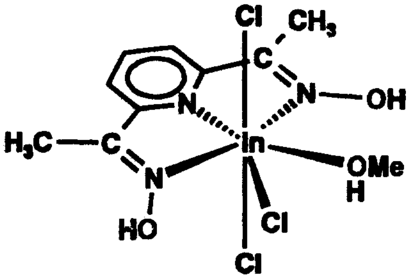
$[InCl_3(L^1)(MeOH)]$ was prepared as reported previously [2]. Na_2mnt was prepared following a litera-

---

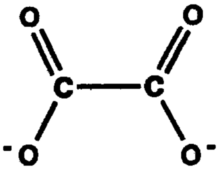
*Author to whom correspondence should be addressed.



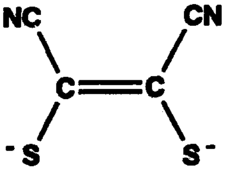
I (L¹)



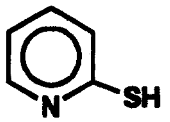
II



III



IV



V

ture procedure [3]. K_2ox and Hpythio were purchased commercially (ALDRICH). IR spectra were recorded as KBr pellets on a Perkin–Elmer Specord 75 IR. Mass spectra were obtained on a MAT TSQ-70 spectrometer (Finnigan). For FAB measurements xenon was used as the primary beam gas. The ion gun was operated at 8 kV and 100 μA (probe temperature: 30°C), nitrobenzylalcohol was used as matrix.

[In(L^1)Cl(ox)(OH_2)]

[$InCl_3$(L^1)(MeOH)] (223 mg, 0.5 mmol) was dissolved in warm MeOH (100 cm^3) and after cooling to room temperature K_2ox (83 mg, 0.5 mmol) in a minimum amount of water was slowly added. The mixture was stirred for 1 h and filtered to remove a small amount of KCl. Colourless crystals of [In(L^1)Cl(ox)(OH_2)] which were suitable for X-ray crystallography deposited upon slow evaporation of the solvent. A second crop of product was obtained by a complete removal of the solvent and extracting the remaining solid with hot MeOH. Colourless crystals, yield: 80%. Found: C, 29.9; H, 2.0; N, 8.1; Cl, 7.6. $C_{11}H_{13}N_3O_7ClIn$ requires: C, 29.4; H, 2.3; N, 7.9; Cl, 7.9%. IR: ν(OH) 3503, 3296, ν(C=O) 1703, 1676, ν(C=N) 1477 cm^{-1}.

[In(L^1)Cl(mnt)]

[$InCl_3$(L^1)(MeOH)] (223 mg, 0.5 mmol) was dissolved in warm MeOH (*ca* 100 cm^3) and the solution was allowed to cool to room temperature. Na_2mnt (93 mg, 0.5 mmol) in MeOH was added dropwise and the mixture was stirred for 1 h at room temperature. During this time, NaCl deposited which was removed by filtration. The filtrate was reduced in volume to *ca* 25 cm^3 and placed in a refrigerator. Yellow crystals of [In(L^1)Cl(mnt)] deposited upon standing overnight. More product was obtained by a further evaporation of the solvent. Yield: 55%. Found: C, 33.0; H, 3.0, N, 14.4; S, 13.0; Cl 7.4. $C_{13}H_{11}N_5O_2S_2ClIn$ requires: C, 32.3; H, 2.3; N, 14.5; S, 13.3; Cl 7.3%. IR: ν(OH) 3285, ν(C=N) 1451, ν(C≡N) 2207, ν(C=C) 1596 cm^{-1}. FAB^+ MS: $m/z = 448$ ([In(L^1)(mnt)]$^+$), $m/z = 308$ ([In(L^1)]$^+$).

[In(pythio)$_3$]

(a) [$InCl_3$(L^1)(MeOH)] (223 mg, 0.5 mmol) was dissolved in warm MeOH (*ca* 100 cm^3) and Hpythio (55 mg, 0.5 mmol) was added. Upon stirring overnight an almost colourless solid deposited which was isolated by filtration and washed with water. Recrystallization from $CHCl_3$/MeOH gave pale yellow crystals of [In(pythio)$_3$] (yield: 25%). Evaporation of the solvent gave considerable amounts of essentially unchanged [$InCl_3$(L^1)(MeOH)]. The [In(pythio)$_3$] yield could be considerably increased (>90%) by choosing an [$InCl_3$(L^1)(MeOH)]/Hpythio ratio of 1 : 3.5.

(b) $InCl_3$ (221 mg, 1 mmol) was dissolved in MeOH (20 cm^3) and Hpythio (345 mg, 3.1 mmol) in MeOH (20 cm^3) was added. The mixture was refluxed for 5 min. Upon cooling an almost colourless solid precipitated, which was filtered off and washed with water and a small amount of MeOH. Recrystallization from $CHCl_3$/MeOH gave pale yellow crystals of [In(pythio)$_3$]. Yield: 95%. Found: C, 40.0; H, 2.7; N, 9.7; S, 22.0. $C_{15}H_{12}N_3S_3In$ requires: C, 40.5; H, 2.7; N, 9.4; S, 21.6%. FAB^+ MS: $m/z = 446$ ([M + H]$^+$) $m/z = 445$ (M^+), $m/z = 336$ ([In(pythio)$_2$ + H]$^+$), $m/z = 335$

([In(pythio)$_2$]$^+$), $m/z = 226$ ([In(pythio)] + H]$^+$), $m/z = 225$ ([In(pythio)]$^+$).

X-ray structure determinations

The intensities for the X-ray determinations were collected at -70°C on automated single crystal CAD4 diffractometers (Enraf–Nonius, Delft) using Mo-K_α and Cu-K_α radiation, respectively, with ω-scans. The unit cell dimensions were determined from the angular settings of 25 high-angle reflections. The structures were solved by direct methods (SHELXS86) [4]. Subsequent Fourier-difference map analyses gave the positions of all non-hydrogen atoms. Refinement was performed using SHELXL93 [5] with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen-atom positions have been derived from the final Fourier difference maps and their positions and thermal parameters have been refined. Crystal data and more details of the data collections and refinements are contained in Table 1. Additional information on the structure determinations has been deposited with the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

In a recent paper we demonstrated that the seven-coordinate indium(III) complex [InCl$_3$(L^1)(MeOH)] easily undergoes ligand exchange reactions when exposed to an excess of monodentate ligands [2]. Predominantly the MeOH ligand is readily replaced by other donor solvent molecules or Cl$^-$. Thus, we prepared a number of ligand exchange products and reported the X-ray crystal structures of the seven-coordinate complexes [InCl$_3$(L^1)(OH$_2$)] and [InCl$_4$(L^1)]$^-$. Reactions with the strong chelating ligand Et$_2$dtc$^-$, however, resulted in the formation of the tris chelate [In(Et$_2$dtc)$_3$].

Reactions with other chelating ligands show that the extent of the ligand exchange and the coordination geometry of the resulting complex depend on the individual complexation properties of the applied ligand and the chelate ring size which can be formed. Whereas the potentially monoanionic, four-membered chelate ring ligand pyridine-2-thiolate is able to replace all ligands from [InCl$_3$(L^1)(MeOH)], the dianions oxalate and maleonitriledithiolate (which form five-membered chelate rings) yield mixed-chelate complexes with remaining pyridine-2,6-bis(acetyloxime). The formation of products with more oxalate ligands could not be observed. With mnt^{2-}, however, a large ligand excess (>5) and heating of the reaction mixture leads to the formation of small amounts of the complex anions [In(mnt)$_2$Cl]$^{2-}$ and [In(mnt)$_3$]$^{3-}$, which could be isolated as their tetrabutylammonium salts and detected mass spectrometrically.

[In(L^1)Cl(ox)(OH$_2$)] is a colourless solid which is soluble in methanol/water mixtures. The ν(C=O) frequency of coordinated oxalate can be detected in the IR spectrum at 1703 and 1676 cm^{-1}. Due to the low solubility of the compound we were not able to obtain good quality FAB mass spectra or NMR spectra.

Single crystals of [In(L^1)Cl(ox)(OH$_2$)] suitable for crystallography could be obtained directly from the reaction mixture. The complex crystallizes together with two molecules of solvent water. Figure 1 shows an ORTEP representation [7] of the seven-coordinate complex molecule. The coordination sphere of indium is approximately a pentagonal bipyramid with the chelating ligands forming the equatorial coordination plane. The angle between the axial Cl$^-$ and the OH$_2$ ligands is 174.6(1) and the equatorially coordinated atoms are coplanar within 0.015(3) Å. The indium atom is situated only slightly out of this plane [0.112(2) Å]. Selected bond lengths and angles of [In(L^1)Cl(ox)(OH$_2$)] are summarized in Table 2. The In—Cl bond is slightly longer by 0.055 Å than the mean value of the In—Cl bonds in the starting material [InCl$_3$(L^1)(MeOH)]. No obvious changes in bond lengths of the pyridine oxime ligand can be observed. The N—In—N angles, however, are larger by *ca* 2°. This fits with the O(1)—In—O(2) angle of 74.2(2)°, which indicates less steric requirements for the coordinated oxalate compared with Cl$^-$ and MeOH in [InCl$_3$(L^1)(MeOH)].

In contrast to the reaction of [InCl$_3$(L^1)(MeOH)] with potassium oxalate that with Na$_2$mnt gave a six-coordinate complex of the composition [In(L^1)Cl(mnt)]. The pale yellow compound is only slightly soluble in most organic solvents. It dissolves sufficiently in dimethylsulfoxide. In this solvent, however, a rapid decomposition can be observed. The IR spectrum of [In(L^1)Cl(mnt)] shows intense bands at 2207 cm^{-1}, indicating the ν(C≡N) vibrations of the dithiolene ligand. The band at 1596 cm^{-1} is characteristic for the ν(C=C) vibrations of coordinated mnt^{2-} [8]. As a consequence of the low solubility of [In(L^1)Cl(mnt)] its FAB$^+$ spectrum shows only a few metal-containing peaks. Besides the molecular ion at $m/z = 448$, only a signal for the fragment [InL^1]$^+$ could be assigned unambiguously.

[In(L^1)Cl(mnt)] crystallizes together with a molecule of solvent MeOH in the rhombohedral space group $R\bar{3}$ with 18 molecules in the unit cell. A representation of the molecular structure is given in Fig. 2. Selected bond lengths and angles are summarized in Table 3. The coordination sphere of indium significantly deviates from the ideal octahedron. This is due to the restricted bite of the almost planar tridentate ligand. The N(1)—In—N(2) angle is 137.1(2)°, which is only larger by 0.4° compared with the corresponding angle in the seven-coordinate [In(L^1)Cl(ox)(OH$_2$)], where the bidentate oxalato ligands is present in the equatorial plane of the pentagonal bipyramide. Markedly smaller N(1)—In—N(2) angles have been observed recently for seven coordinate indium(III) complexes of L^1 with

Table 1. X-ray structure data collection and refinement parameters

	$[In(L^1)Cl(ox)(OH_2)]\cdot 2H_2O$	$[In(L^1)Cl(mnt)]\cdot MeOH$	$[In(pythio)_3]$
Crystal dimensions (mm^3)	0.25 × 0.1 × 0.05	0.3 × 0.05 × 0.05	0.2 × 0.2 × 0.15
Formula	$C_{11}H_{17}N_3O_9ClIn$	$C_{14}H_{15}N_5ClO_3S_2In$	$C_{15}H_{12}N_3S_3In$
M	485.55	515.70	445.28
Crystal system	Monoclinic	Rhombohedral	Monoclinic
Space group	$P2_1/n$	$R\bar{3}$	$P2_1$
Unit cell	$a = 8.829(4)$ Å	$a = 26.916(2)$ Å	$a = 8.807(6)$ Å
	$b = 20.707(6)$ Å	$b = 26.916(2)$ Å	$b = 11.730(2)$ Å
	$c = 9.363(4)$ Å	$c = 14.308(1))$Å	$c = 9.416(8)$ Å
	$\alpha = 90°$	$\alpha = 90°$	$\alpha = 90°$
	$\beta = 101.43(3)°$	$\beta = 90°$	$\beta = 114.77(3)°$
	$\gamma = 90°$	$\gamma = 120°$	$\gamma = 90°$
V (Å^3)	1678(1)	8977(1)	883(1)
Z	4	18	2
D_c(g cm^{-3})	1.922	1.717	1.674
Radiation/(λ)	Cu-K_α/1.54184 Å	Cu-K_α/1.54184 Å	Mo-K_α/0.71073 Å
Linear absorption coefficient (mm^{-1})	13.231	12.878	1.690
Absorption correction	DIFABS	ψ scans	None
T_{min}	0.228	0.9677	
T_{max}	1.000	0.9973	
Weighting scheme [$P = (F_0^2+2F_c^2)/3$]	$w = 1/[\sigma^2(F_0^2) + (0.0723\ P)^2 + 2.9109\ P]$	$w = 1/[\sigma^2(F_0^2) + (0.0608P)^2 + 93.2852P]$	$w = 1/[\sigma^2(F_0^2) + (0.0324P)^2]$
Measured reflections	2853	4406	5290
Independent reflections	2378	3180	2652
Independent reflections [$I > 2\sigma(I)$]	2050	2405	2120
Refined parameters	294	295	247
$R_1(F)/wR_2(F^2)$	0.0399/0.1050	0.0497/0.1175	0.0301/0.0644
GoF	1.057	1.056	1.037
Programs used	SHELXS86 [4], SHELXL93 [5], PLATON, HELENA [9]	SDP [16], SHELXS86 [4], SHELXL93 [5], PLATON, HELENA [6]	SHELXS86 [4], SHELXL93 [5], PLATON, HELENA [6]

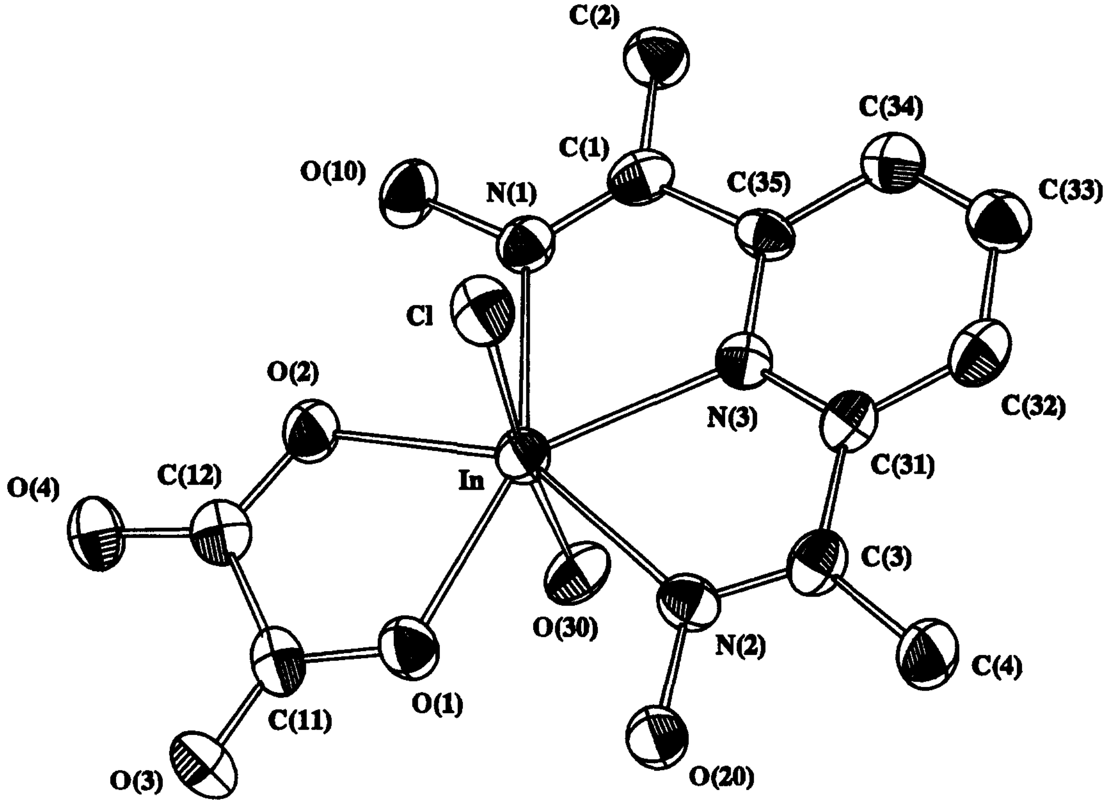


Fig. 1. Molecular structure [7] of $[In(L^1)Cl(ox)(OH_2)]$ along with the atomic numbering scheme. Thermal ellipsoids represent 50% probability.

monodentate co-ligands [2]. The larger bite angles in the mixed-chelate complexes correspond with shorter In—N(amine) bond lengths by *ca* 0.08 Å. Despite the bonding situation in $[In(L^1)Cl(ox)(OH_2)]$, only one donor atom of the chelating mnt^{2-} occupies an equatorial position. The plane which is formed by the atoms N(1), N(2), N(3) and In is coplanar within 0.063(8) Å. The bonding situation within the mnt^{2-} ligand shows no unusual features and can be compared with those in other indium(III) complexes with maleonitrildithiolate [9,10]. Small differences in the In—S bond lengths indicated a somewhat weaker *trans* influence of Cl^- compared with the nitrogen atom of the pyridine ring.

Whereas with the dianionic ligands ox^{2-} and mnt^{2-}, which both are able to form five-membered chelate rings, mixed chelate complexes could be isolated, the reaction of $[InCl_3(L^1)(MeOH)]$ with pyridine-2-thiol gives the tris-chelate $[In(pythio)_3]$. This behavior of a monoanionic ligand which is able to form only four-membered chelate rings well resembles with that of diethyldithiocarbamate (Et_2dtc^-), the reaction of which with $[InCl_3(L^1)(MeOH)]$ has been described previously and preferably gives the tris chelate $[In(Et_2dtc)_3]$ [2].

$[In(pythio)_3]$ is formed very easily from the reaction of $[InCl_3(L^1)(MeOH)]$ with Hpythio. The compound crystallizes directly from the reaction mixture. A more versatile approach is that from indium chloride. Our experimental results completely agree with those of Barron and co-workers who reported the synthesis of $[In(pythio)_3]$ in a very recent paper [11]. Recrystallization from $CHCl_3$/MeOH gives pale-yellow blocks which are readily soluble in CH_2Cl_2, $CHCl_3$ or benzene. The FAB^+ mass spectrum shows a peak (20% B) at $m/z = 445$, which represents the molecular ion peak of the compound. Main fragments can be assigned to $[In(pythio)_2]^+$ ($m/z = 335$) and $[In(pythio)]^+$ ($m/z = 225$). All these three peaks are accompanied by signals at $m/z + 1$, which confirms the possibility of the formation of protonated species of the coordinated ligand after cleavage of the chelate ring [12].

The crystal structure of $[In(pythio)_3]$ confirms that the ligand is deprotonated and acts as a chelator. With this, the indium compound has similar structural features like the corresponding antimony compound [13] and contrasts with complexes where a monodentate coordination as pyridinethiolate-*S* [14] or pyridiniumthiolate-*S* [15] is preferred. Figure 3 shows an ORTEP representation of the neutral complex molecule. Table 4 contains selected bond lengths and angles. The coordination sphere of the indium can be described as a strongly distorted octahedron. The ligands show a facial arrangement with respect to their donor atoms. Steric restrictions caused by the

Table 2. Selected bond lengths and angles in $[In(L^1)Cl(ox)(OH_2)] \cdot 2\,H_2O$

In—Cl	2.451(2)	O(4)—C(12)	1.225(7)
In—O(1)	2.171(4)	C(11)—C(12)	1.55(1)
In—O(2)	2.184(4)	N(1)—O(10)	1.393(7)
In—N(1)	2.326(6)	N(1)—C(1)	1.283(7)
In—N(2)	2.344(5)	N(2)—O(20)	1.387(7)
In—N(3)	2.286(5)	N(2)—C(3)	1.282(7)
In—O(30)	2.201(5)	N(3)—C(31)	1.345(8)
O(1)—C(11)	1.297(7)	N(3)—C(35)	1.341(8)
O(2)—C(12)	1.286(7)	C(1)—C(35)	1.501(9)
O(3)—C(11)	1.222(7)	C(3)—C(31)	1.474(9)
Cl—In—O(1)	95.9(1)	O(30)—In—N(3)	84.8(2)
Cl—In—O(2)	95.5(1)	N(1)—In—N(2)	136.7(2)
Cl—In—O(30)	174.6(1)	N(1)—In—N(3)	68.6(2)
Cl—In—N(1)	90.1(1)	N(2)—In—N(3)	68.2(2)
Cl—In—N(2)	91.5(1)	C(11)—O(1)—In	118.4(4)
Cl—In—N(3)	89.9(1)	C(12)—O(2)—In	118.1(4)
O(1)—In—O(2)	74.2(2)	O(1)—C(11)—C(12)	114.3(5)
O(1)—In—O(30)	89.0(2)	O(2)—C(12)—C(11)	114.9(5)
O(1)—In—N(1)	147.9(2)	C(1)—N(1)—In	121.9(5)
O(1)—In—N(2)	74.5(2)	C(3)—N(2)—In	121.2(5)
O(1)—In—N(3)	142.4(2)	C(31)—N(3)—In	119.4(4)
O(2)—In—O(30)	88.1(2)	C(35)—N(3)—In	119.7(4)
O(2)—In—N(1)	73.9(2)	N(3)—C(31)—C(3)	116.2(5)
O(2)—In—N(2)	148.5(2)	N(3)—C(35)—C(1)	115.7(5)
O(2)—In—N(3)	142.2(2)	N(1)—C(1)—C(35)	113.3(6)
O(30)—In—N(1)	85.9(2)	N(2)—C(3)—C(31)	114.2(6)
O(30)—In—N(2)	87.6(2)		

Table 3. Selected bond lengths (Å) and angles (°) in $[In(L^1)Cl(mnt)] \cdot MeOH$

In—Cl	2.420(2)	N(1)—O(10)	1.393(8)
In—S(1)	2.511(2)	N(1)—C(1)	1.28(1)
In—S(2)	2.534(2)	N(2)—O(20)	1.373(8)
In—N(1)	2.357(6)	N(2)—C(3)	1.28(1)
In—N(2)	2.351(6)	N(3)—C(31)	1.356(9)
In—N(3)	2.280(6)	N(3)—C(35)	1.350(9)
S(1)—C(11)	1.736(8)	C(1)—C(35)	1.49(1)
S(2)—C(12)	1.720(9)	C(3)—C(31)	1.46(1)
C(11)—C(12)	1.37(1)		
Cl—In—S(1)	169.78(8)	N(2)—In—N(3)	69.1(2)
Cl—In—S(2)	89.32(7)	C(11)—S(1)—In	99.1(3)
Cl—In—N(1)	96.2(2)	C(12)—S(2)—In	98.6(3)
Cl—In—N(2)	88.6(2)	S(1)—C(11)—C(12)	126.8(7)
Cl—In—N(3)	94.1(2)	S(2)—C(12)—C(11)	127.7(6)
S(1)—In—S(2)	86.80(7)	C(1)—N(1)—In	121.8(5)
S(1)—In—N(1)	92.9(2)	C(3)—N(2)—In	119.3(5)
S(1)—In—N(2)	87.9(2)	C(31)—N(3)—In	118.7(5)
S(1)—In—N(3)	93.7(2)	C(35)—N(3)—In	120.3(5)
S(2)—In—N(1)	84.7(2)	N(3)—C(31)—C(3)	116.3(6)
S(2)—In—N(2)	138.1(2)	N(3)—C(35)—C(1)	116.0(7)
S(2)—In—N(3)	152.7(2)	N(1)—C(1)—C(35)	113.6(7)
N(1)—In—N(2)	137.1(2)	N(2)—C(3)—C(31)	116.2(7)
N(1)—In—N(3)	68.0(2)		

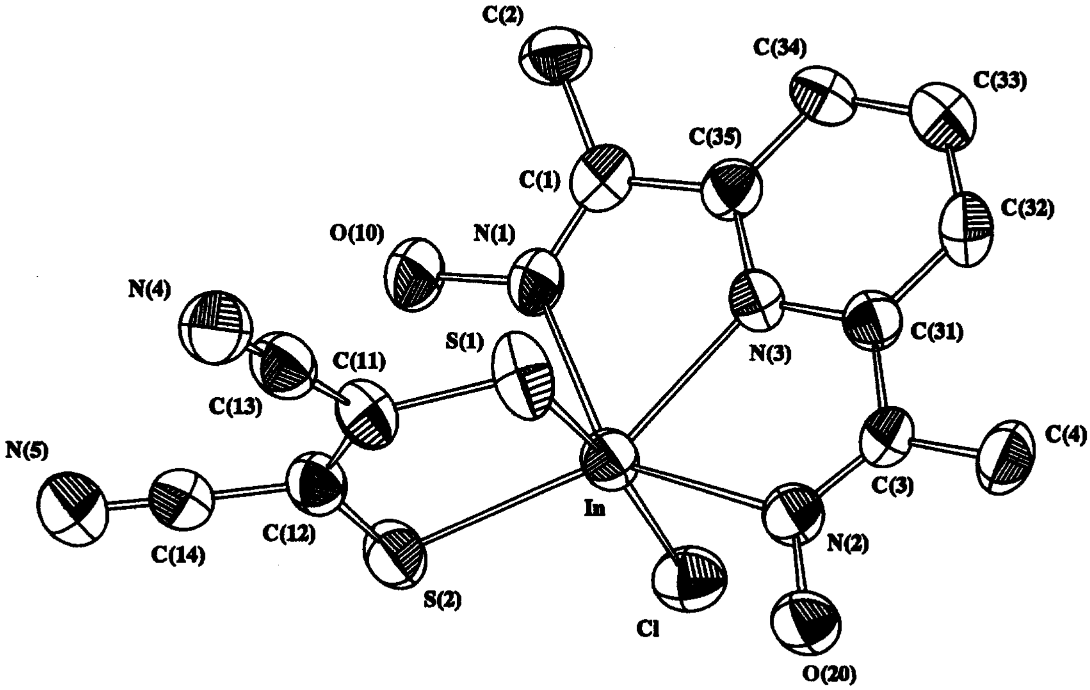


Fig. 2. Molecular structure [7] of $[In(L^1)Cl(mnt)]$ along with the atomic numbering scheme. Thermal ellipsoids represent 50% probability.

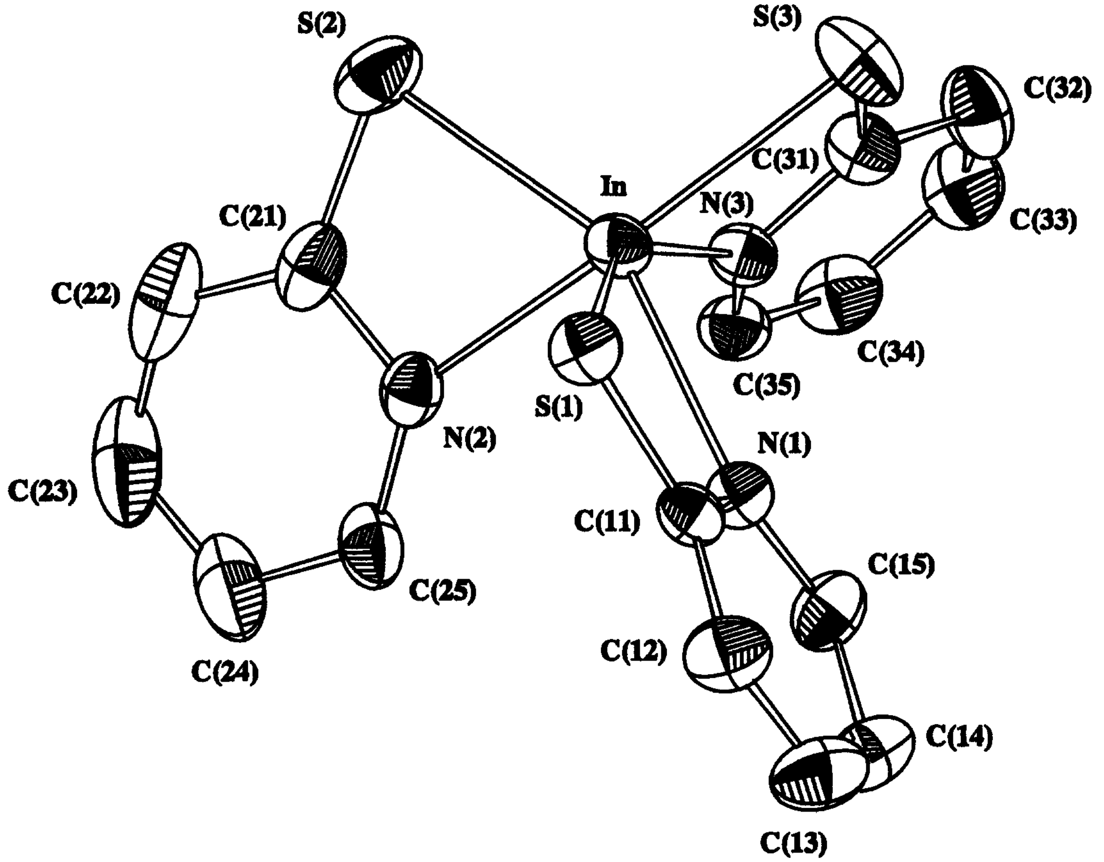


Fig. 3. Molecular structure [7] of [In(pythio)$_3$] along with the atomic numbering scheme. Thermal ellipsoids represent 50% probability.

Table 4. Selected bond lengths (Å) and angles (°) in [In(pythio)$_3$]

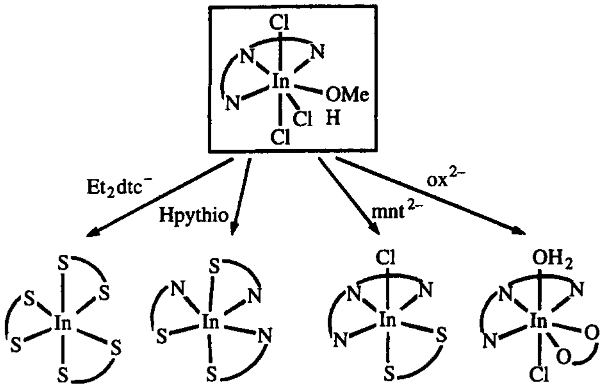
In—S(1)	2.537(2)	S(1)—C(11)	1.737(6)
In—S(2)	2.533(2)	S(2)—C(21)	1.754(9)
In—S(3)	2.533(2)	S(3)—C(31)	1.74(1)
In—N(1)	2.314(4)	N(1)—C(11)	1.342(6)
In—N(2)	2.283(5)	N(2)—C(21)	1.336(7)
In—N(3)	2.306(5)	N(3)—C(31)	1.35(1)
S(1)—In—S(2)	108.42(8)	N(1)—In—N(2)	88.4(2)
S(1)—In—S(3)	111.39(7)	N(1)—In—N(3)	87.3(2)
S(2)—In—S(3)	106.7(1)	N(2)—In—N(3)	88.8(2)
S(1)—In—N(1)	64.5(1)	C(11)—S(1)—In	81.6(2)
S(1)—In—N(2)	96.7(1)	C(21)—S(2)—In	80.8(2)
S(1)—In—N(3)	151.1(1)	C(31)—S(3)—In	81.2(2)
S(2)—In—N(1)	152.1(1)	S(1)—C(11)—N(1)	114.3(3)
S(2)—In—N(2)	65.1(2)	S(2)—C(21)—N(2)	113.8(5)
S(2)—In—N(3)	99.8(2)	S(3)—C(31)—N(3)	115.0(4)
S(3)—In—N(1)	100.8(1)	C(11)—N(1)—In	99.3(3)
S(3)—In—N(2)	151.7(1)	C(21)—N(2)—In	100.2(4)
S(3)—In—N(3)	65.2(2)	C(31)—N(3)—In	98.6(4)

S—C—N bite angles of the ligands which are *ca* 65° are responsible for the distortions from the ideal octahedral symmetry. Thus, the N—In—N angles are approximately 88°. The S—In—S angles, however, have been found between 106.7 and 111.4°. The S—C bond lengths of approximately 1.74 Å range between typical sulfur–carbon single and double bonds and reflect considerable delocalization of electron density in the chelate rings. No unusual structural features have been found inside the organic ligands.

SUMMARY

It has been demonstrated that [InCl$_3$(L^1)(MeOH)] undergoes ligand exchange reactions with chelating ligands. Mixed-chelate complexes are formed with dianionic ligands as oxalate or maleonitrildithiolate which are able to build five-membered chelate rings. Further ongoing ligand exchange was achieved when pyridine-2-thiole was used, finally giving [In(pythio)$_3$] with three deprotonated pyridine-2-thiolate ligands forming four-membered chelate rings. Scheme I summarizes the experimental results.

The structural studies in the present paper, together with those in [2] show that pyridine-2,6-bis(acetyloxime) is a ligand with a very rigid skeleton. This limits first of all the possible N(oxime)—In—N(oxime) angle. Values between 131.3 and 136.7° have been found for the seven-coordinate



Scheme I.

indium complexes. The formation of a distorted octahedral coordination sphere around indium leads to an N(1)—In—N(2) angle which is larger by only 0.5°. Thus, the composition of the coordination sphere and the coordination geometry in the complexes under study are mainly dominated by the coordination properties of the tridentate ligand.

Acknowledgements—The work was financially supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. SA gratefully acknowledges a grant of the University of Tübingen. We wish to express our thanks to Professor J. Strähle (Tübingen) for providing us with facilities and for his kind hospitality.

REFERENCES

1. Shearer, H. M. M., Twiss, J. and Wade, K., *J. Organomet. Chem.* 1980, **184**, 309.
2. Abram, S., Maichle-Mössmer, C. and Abram, U., *Polyhedron*, in press.
3. Bähr, G. and Schleitzer, G., *Chem. Ber.* 1957, **90**, 438.
4. Sheldrick, G. M., *SHELXS86. A Program for the Solution of X-ray Structures.* University of Göttingen, Germany, 1986.
5. Sheldrick, G. M., *SHELXL93. A Program for the Refinement of X-ray Structures.* University of Göttingen, Germany, 1993.
6. Spek, A., *PLATON, HELENA. Programs for Data Reduction and Calculation on X-ray Data.* University of Utrecht, The Netherlands, 1994.
7. Zsolnai, L., *ZORTEP. A Program for the Ellisoid Presentation of X-ray Structure Results.* University of Heidelberg, Germany, 1994.
8. Maki, A. H., Edelstein, N., Davison, A. and Holm, R. H., *J. Am. Chem. Soc.* 1964, **86**, 4580.
9. Einstein, F. W. B. and Jones, R. D. G., *J. Chem. Soc. A*, 1971, 2782.
10. Day, R. D. and Holmes, R. R., *Inorg. Chem.* 1982, **21**, 2379.
11. Landry, C. C., Hynes, A., Barron, A. R., Haiduc, I. and Silvestru, C., *Polyhedron*, 1996, **15**, 391.
12. Raper, E. S., *Coord. Chem. Rev.* 1996, **153**, 199.
13. Bozopoulos, A. P., Kokkou, S. C., Rentzeperis, P. J. and Karagannidis, P., *Acta Cryst.* 1984, **C40**, 944.
14. Cookson, P. D. and Tiekink, E. R. T., *J. Chem. Soc. Dalton Trans.* 1993, 259.
15. Mack, J. and Abram, U., unpublished.
16. Frenz, A., *VAXSDP. Structure Determination Package*, Version 3.0. College Station, Texas and Enraf–Nonius, The Netherlands. (1984)