Pergamon

Polyhedron Vol. 16, No. 13, pp. 2183–2191, 1997
© 1997 Elsevier Science Ltd
All rights reserved. Printed in Great Britain
0277–5387/97 \$17.00+0.00

PII: S0277–5387(96)00553–0

Indium(III) complexes with tridentate nitrogen donor ligands. Synthesis, characterization and crystal structure of complexes with pyridine-2,6-bis(acetyloxime) and 2,6-bis (1-phenyliminoethyl)pyridine

Sonja Abram,* Cäcilia Maichle-Mössmer and Ulrich Abram

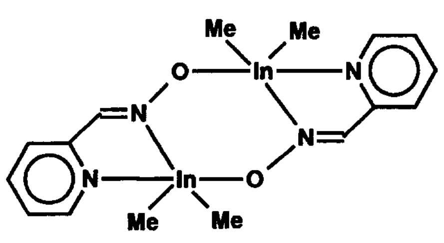
Institute of Inorganic Chemistry, University of Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany

(Received 10 September 1996; accepted 13 November 1996)

Abstract—2,6-Bis(acetyloxime)pyridine, 2,6-$C_5H_3N(C_2H_3NOH)_2$ (L^1), reacts with indium(III) chloride in methanol to give the seven-coordinate complex [$InCl_3(L^1)(MeOH)$]. The structurally similar Schiff base ligand 2,6-bis(1-phenyliminoethyl)pyridine (L^2), 2,6-$C_5H_3N(C_2H_3NC_6H_5)_2$, however, forms a six-coordinate indium(III) complex of the composition [$InCl_3(L^2)$]. The In—N bond distances are longer by 0.03–0.12 Å in the seven-coordinate compound compared with those in the Schiff base complex. The MeOH ligand in [$InCl_3(L^1)(MeOH)$] can be replaced by Cl^- or H_2O to give the complex anion [$InCl_4(L^1)$]$^-$ and [$InCl_3(L^1)(OH_2)$], respectively. The pentagonal-bipyramidal coordination environment of the metal is preserved during these reactions. © 1997 Elsevier Science Ltd

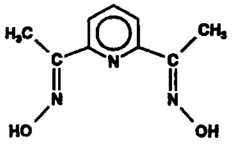
Keywords: indium complexes; oximes; nitrogen donor ligands; crystal structure.

Structural studies of indium complexes with oxime ligands are only rarely reported [1]. The structure of a dimeric compound which is obtained from the reaction of $InMe_3$ and pyridine-2-carbaldehyde oxime has been elucidated as a dimer with deprotonated ligands (I). The coordination sphere of indium in the compound is described as a strongly distorted trigonal bipyramid [1]. Deprotonation of the oxime enables the ligand to become tridentate and to bridge two metal centres.

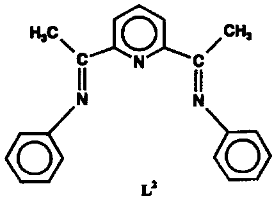


I

In our systematic studies on the coordination behaviour of indium(III) we investigated the reaction of $InCl_3$ with pyridine-2,6-bis(acetyloxime) L^1 and the structurally similar Schiff base ligand 2,6-bis(1-phenyliminoethyl)pyridine L^2. The oxime complex obtained is a good precursor for the synthesis of new indium(III) mixed-ligand complexes. Some reactions with monodentate ligands and the structures of the products are herein described.



L^1



L^2

EXPERIMENTAL

$InCl_3$ and 2,6-diacetylpyridine were purchased from Aldrich. IR spectra were recorded as KBr pellets on

---

* Author to whom correspondence should be addressed.

a Perkin Elmer Specord 75 IR. Mass spectra were recorded on a MAT TSQ-70 spectrometer (Finnigan). For FAB measurements xenon was used as primary beam gas. The ion gun was operated at 8 kV and 100 μA (probe temperature: 30°C), nitrobenzylalcohol was used as matrix. NMR spectra were recorded in $CDCl_3$ solutions on a Bruker AM 400 spectrometer (TMS as internal standard).

L^1. Pyridine-2,6-bis(acetyloxime) was prepared by a routine procedure for the synthesis of oximes [2] from 2,6-diacetylpyridine, hydroxylamine hydrochloride and triethylamine in a $MeOH/H_2O$ mixture. Colourless solid. Found: C, 56.3; H, 5.9; N, 21.7; $C_9H_{11}N_3O_2$ requires: C, 55.9; H, 5.7; N, 21.7%. EI^+ MS: $m/z = 193$ (M^+).

L^2. 1.63 g (10 mmol) 2,6-diacetylpyridine were dissolved in 100 cm^3 ethanol and excess (about 30 mmol) aniline was added dropwise. The mixture was heated under reflux for 1 h and the solvent was removed *in vacuo* giving a yellow, highly viscous oil. This residue was redissolved in hot diethylether. Upon cooling yellow crystals deposited which were filtered off and washed with cold diethylether. More product could be obtained by slow evaporation of the filtrate. Yellow needles. Yield 80%. Found: C, 80.5; H, 6.2; N, 13.2; $C_{21}H_{19}N_3$ requires: C, 80.5; H, 6.1; N, 13.4%. EI^+ MS: $m/z = 313$ (M^+).

$[InCl_3(L^1)(MeOH)]$. 193 mg (1 mmol) L^1 were dissolved in 25 cm^3 methanol and a methanolic solution of 220 mg (1 mmol) $InCl_3$ was added dropwise. The colourless reaction mixture was heated under reflux for 1.5 h and the volume was reduced to about 15 cm^3. After standing overnight, colourless crystals deposited which were recrystallized from methanol. Yield: 70%. Found: C, 26.0; H, 3.7; N, 9.6; $C_{10}H_{15}N_3O_3Cl_3In$ requires: C, 26.9; H, 3.4; N, 9.4%. FAB^+ MS: $m/z = 378$ ($[InCl_2(L^1)]^+$).

$[InCl_3(L^2)] \cdot CH_3CN$. 313 mg (1 mmol) L^2 were dissolved in 35 cm^3 warm CH_3CN and 220 mg (1 mmol) $InCl_3$ in acetonitrile were added dropwise. After heating under reflux for 2 h the volume was reduced to about 15 ml. Upon cooling and standing in a refrigerator yellow crystals deposited which were filtered off and recrystallized from CH_3CN. Yield: 84%. Found: C, 46.9; H, 3.3; N, 9.8; $C_{23}H_{22}N_4Cl_3In$ requires: C, 48.0; H, 3.8; N, 9.7%. FAB^+ MS $m/z = 499$ ($[InCl_2(L^2)]^+$).

$[InCl_3(L^1)(OH_2)]$. 445 mg (1 mmol) $[InCl_3(L^1)(MeOH)]$ were dissolved in 100 cm^3 of hot acetone and 10 cm^3 water were added. Upon cooling and slow evaporation of the solvent colourless plates precipitated. Yield: 70%. Found: C, 24.2; H, 3.5; N, 9.7: $C_9H_{13}N_3O_3Cl_3In$ requires: C, 25.0; H, 3.0; N, 9.7%. FAB^+ MS: $m/z = 378$ ($[InCl_2(L^1)]^+$).

$(Ph_4P)[InCl_4(L^1)]$. 44.5 mg (0.1 mmol) $[InCl_3(L^1)(MeOH)]$ were dissolved in 10 cm^3 hot acetone and 0.5 cm^3 conc. HCl was added. The mixture was heated under reflux for 5 min and 37.5 mg (0.1 mmol) Ph_4PCl was added. Upon slow evaporation of the acetone colourless crystals deposited which were recrystallized from acetone/xylene. Yield: 45%. Found: C, 50.0; H, 4.0; N, 5.4; $C_{33}H_{31}N_3O_2Cl_4InP$ requires: C, 50.2; H, 4.0; N, 5.3%.

$(Et_2NH_2)[InCl_4(L^1)]$, $[In(Et_2dtc)_3]$. 445 mg (1 mmol) $[InCl_3(L^1)(MeOH)]$ were dissolved in 100 cm^3 MeOH and 675 mg (3 mmol) $NaEt_2dtc \times 3\ H_2O$ were added. The mixture was stirred for 1 h. Upon slow evaporation a colourless solid of $[In(Et_2dtc)_3]$ precipitated. The volume was reduced to 20 cm^3 and cooled to complete the crystallization of $[In(Et_2dtc)_3]$ (yield: 90%). The compound was characterized by elemental analysis, NMR and mass spectra. The data obtained are consistent with those reported earlier [3]. From the remaining mother liquor a small amount of pale-reddish crystals were deposited upon slow evaporation in a refrigerator which could be characterized as $(Et_2NH_2)[InCl_4(L^1)]$. Yield: about 5%. Found: C, 29.7; H, 4.2; N, 10.4; $C_{13}H_{23}N_4O_2Cl_4In$ requires: C, 29.8; H, 4.4; N, 10.7%.

X-ray structure determinations

The intensities for the X-ray determinations were collected on automated single crystal diffractometers of the type CAD4 (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 Patterson synthesis ($[InCl_3(L^1)(MeOH)]$, $(Et_2NH_2)[InCl_4(L^1)]$) and direct methods ($[InCl_3L^1(OH_2)]$, $[InCl_3(L^2)] \cdot CH_3CN$), respectively, using SHELXS86 [4]. Subsequent Fourier-difference map analyses yielded the positions of the non-hydrogen atoms. Refinement was performed using SHELXL93 [5]. The hydrogen atoms were either included at calculated positions and refined using the "riding model" option of SHELXL93 ($(Et_2NH_2)[InCl_4(L^1)]$) or derived from the Fourier difference map and refined ($[InCl_3(L^1)(MeOH)]$, $[InCl_3(L^2)] \cdot CH_3CN$, $[InCl_3L^1(OH_2)]$). 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 at the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

The tridentate oxime and Schiff base ligands L^1 and L^2 have been found to form stable complexes with indium. The reaction of indium(III) chloride with L^1 in methanol gave airstable, colourless plates of $[InCl_3(L^1)(MeOH)]$ which crystallized directly from the reaction mixture. The IR spectrum of the compound shows the $\nu(C{=}N)$ frequency at 1585 cm^{-1}. No evidence can be found for the molecular ion in the FAB^+ mass spectrum of $[InCl_3(L^1)(MeOH)]$. A peak at $m/z = 378$ which is assigned to the fragment $[InCl_2(L^1)]$ represents the base peak of the spectrum.

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

	$[InCl_3L^1(MeOH)]$	$[InCl_3L^2] \cdot CH_3CN$	$[InCh_3L^1(OH)_2]$	$(Et_2NH_2)[InCl_4(L^1)]$
Crystal dimensions (mm)	0.4 × 0.2 × 0.05	0.6 × 0.25 × 0.2	0.5 × 0.5 × 0.2	0.2 × 0.1 × 0.05
Formula	$C_{10}H_{15}N_3O_3Cl_3In$	$C_{23}H_{22}N_4Cl_3In$	$C_9H_{13}N_3O_3Cl_3In$	$C_{13}H_{23}N_4O_2Cl_4In$
M	446.42	575.62	432.39	523.97
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Measuring temperature (K)	293(2)	208(2)	293(2)	213(2)
a (Å)	8.847(7)	10.069(4)	7.568(2)	7.804(1)
b (Å)	9.152(8)	14.599(2)	9.840(2)	8.545(2)
c (Å)	10.419(8)	16.547(6)	11.158(3)	15.657(4)
α (°)	74.34(6)		73.28(2)	84.99(2)
β (°)	81.84(6)	90.20(2)	72.69(2)	83.60(2)
γ (°)	74.71(6)		72.71(2)	78.66(2)
V (Å^3)	781(1)	2432(1)	739.2(3)	1015.0(4)
Z	2	4	2	2
D_c (g cm^{-3})	1.898	1.572	1.943	1.714
Radiation/(λ) (Å)	Mo-K_α/0.71073	Mo-K_α/0.71073	Mo-K_α/0.71073	Cu-K_α/1.54184
Linear absorption coefficient (mm^{-1})	2.034	1.319	2.146	14.274
Absorption correction	None	None	None	Ψ scans
T_{min}				0.8542
T_{max}				0.9368
Weighting scheme ($P = (F_o^2 + 2F_c^2)/3$)	$w = 1/[\sigma^2(F_o^2) + (0.0629\,P)^2 + 0.3448\,P]$	$w = 1/[\sigma^2(F_o^2) + (0.0308P)^2 + 0.7570P]$	$w = 1/[\sigma^2(F_o^2) + (0.0363P)^2 + 0.1760P]$	$w = 1/[\sigma^2(F_o^2) + 0.0729P)^2 + 4.2130P]$
Measured reflections	4848	6848	4328	3238
Independent reflections	4111	5874	3536	2554
Independent reflections ($I > 2\sigma(I)$)	3554	4557	2983	2191
Refined parameters	241	368	224	218
R_1 (F)/$wR2$(F^2)	0.0508/0.1047	0.0306/0.0642	0.0300/0.0673	0.0493/0.1270
GoF	1.086	1.030	1.059	1.132
Programs used	SHELXS86 [4], SHELXL93 [5], PLATON, HELENA [9]	SHELXS86 [4], SHELXL93 [5], PLATON, HELENA [9]	SHELXS86 [4], SHELXL93 [5], PLATON, HELENA [9]	SDP [10], SHELXS86 [4], SHELXL93 [5], PLATON, HELENA [9], HKL [11]

Other metal containing fragments cannot be observed with significant intensities.

An X-ray structure determination proved a distorted pentagonal-bipyramidal coordination sphere for the indium atom. The donor atoms of the tridentate ligand, Cl(3) and O(30) are coplanar within 0.041 Å. Fig. 1 represents an ORTEP plot of the complex molecule together with the atomic numbering scheme. Corresponding bond lengths and angles are summarized in Table 2. The axial In—Cl bond distances of 2.396 Å are equal within their standard deviations, whereas the In—Cl(3) bond of 2.587 Å is

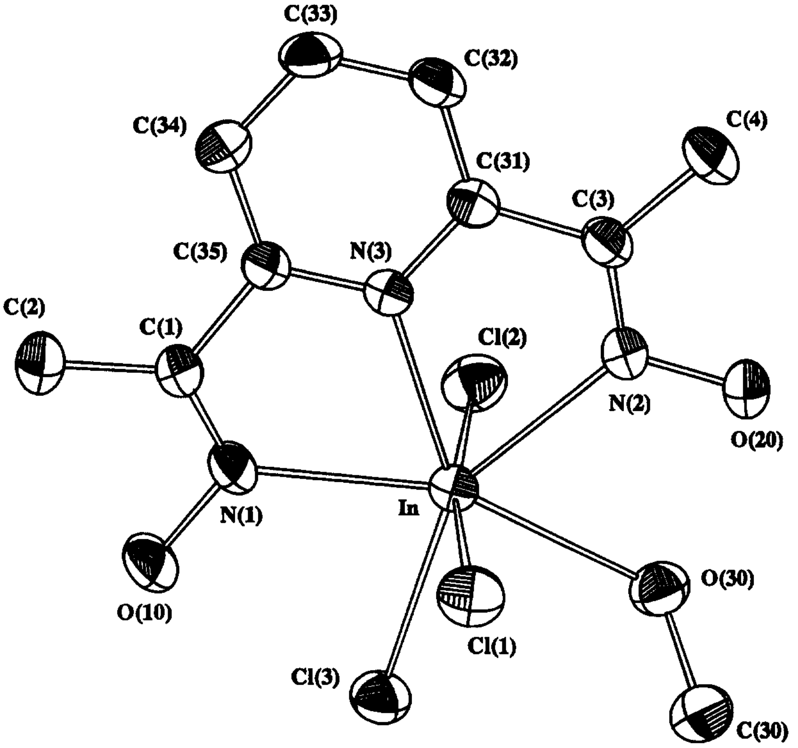


Fig. 1. Molecular structure of $[InCl_3(L^1)(MeOH)]$ along with the atomic numbering scheme.

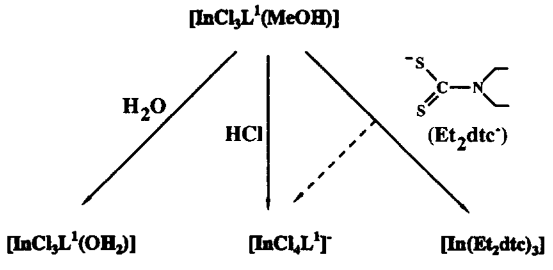
Table 2. Selected bond lengths (Å) and angles (°) in $[InCl_3(L^1)(MeOH)]$

In—Cl(1)	2.369(3)	N(1)—O(10)	1.374(4)
In—Cl(2)	2.397(3)	N(1)—C(1)	1.273(5)
In—Cl(3)	2.587(2)	N(2)—O(20)	1.372(4)
In—N(1)	2.374(4)	N(2)—C(3)	1.279(5)
In—N(2)	2.399(3)	N(3)—C(31)	1.348(5)
In—N(3)	2.369(3)	N(3)—C(35)	1.341(5)
In—O(30)	2.528(4)	C(1)—C(35)	1.480(5)
		C(3)—C(31)	1.480(5)
Cl(1)—In—Cl(2)	170.24(4)	N(3)—In—Cl(2)	90.3(1)
Cl(1)—In—Cl(3)	90.39(8)	N(3)—In—Cl(3)	145.32(8)
Cl(1)—In—O(30)	89.1(1)	N(3)—In—O(30)	137.0(1)
Cl(1)—In—N(2)	88.01(1)	N(3)—In—N(1)	66.5(1)
Cl(2)—In—Cl(3)	91.41(8)	N(3)—In—N(2)	66.3(1)
Cl(2)—In—O(30)	81.9(1)	O(30)—In—Cl(3)	77.44(9)
Cl(2)—In—N(2)	85.5(1)	O(10)—N(1)—In	123.1(2)
N(1)—In—Cl(1)	93.4(1)	O(20)—N(2)—In	122.9(2)
N(1)—In—Cl(2)	96.3(1)	N(1)—C(1)—C(35)	114.8(3)
N(1)—In—Cl(3)	78.9(1)	N(2)—C(3)—C(31)	114.9(3)
N(1)—In—O(30)	156.2(1)	N(3)—C(31)—C(3)	115.8(3)
N(1)—In—N(2)	132.8(1)	N(3)—C(35)—C(1)	115.7(3)
N(2)—In—Cl(3)	148.36(8)	C(1)—N(1)—In	122.8(2)
N(2)—In—O(30)	70.9(1)	C(3)—N(2)—In	122.5(3)
N(3)—In—Cl(1)	93.6(1)		

significantly longer. Only slight differences have been found for the indium–nitrogen bond lengths. Due to the restricting bite angle of the amine oxime ligand the N—In—N angles are small at about 66°. This may also be a reason for the formation of a seven-coordinate complex.

In contrast to the ligand L^1, the Schiff base L^2 reacts with $InCl_3$ to yield the six-coordinate complex $[InCl_3(L^2)]$. Yellow crystals of this compound were formed when the reactants were heated under reflux in CH_3CN. The IR spectrum shows the $\nu(C{=}N)$ bond at 1620 cm^{-1}. Mass spectral studies on the product gave no evidence for the molecular ion. The base peak in the FAB^+ spectrum at $m/z = 499$ can be assigned to $[InCl_2(L^2)]^+$. Further fragmentation goes along with stepwise loss of Cl^-.

A single crystal of $[InCl_3(L^2)]$ suitable for X-ray crystallography could be obtained from slow cooling of a hot CH_3CN solution of the complex. $[InCl_3(L^2)]$ crystallizes along with one molecule of solvent acetonitrile in the monoclinic space group $P2_1/c$. An ORTEP [6] representation of the molecule is given with Fig. 2. Table 3 contains selected bond lengths and angles. The most significant difference to the structure of the amine oxime complex discussed above is the distorted octahedral coordination sphere of the indium atom in the Schiff base compound. This is caused by the bulky phenyl groups which prevent the coordination of a fifth ligand in the equatorial sphere and the N—In—N angles which have been held to be responsible for the pentagonal equatorial plane in $[InCl_3(L^1)(MeOH)]$. They are larger by about 4° in the six-coordinate Schiff base complex. With this, an overall bite angle of the tridentate Schiff base of 141.5(1)° can be observed *vs* 132.8(1)° in the corresponding amine oxime ligand. As a consequence of this general feature the In—N bonds in $[InCl_3(L^2)]$ are shorter by about 0.1 Å compared with the values in $[InCl_3(L^1)(MeOH)]$. A similar observation can be made at the In—Cl bonds. In the six-coordinate $[InCl_3(L^2)]$, the equatorial In—Cl(3) bond is shorter by 0.06 Å than the axial In—Cl(1) and In—Cl(2) bonds. This is in contrast to the seven-coordinate $[InCl_3(L^1)(MeOH)]$ where the sterically overloaded equatorial coordination sphere causes an In—Cl(3) bond distance of 2.587(2) Å. The equatorial coordination spheres in both complexes are almost planar with maximum deviations of 0.041 Å ($[InCl_3(L^1)(MeOH)]$) and 0.043 Å ($[InCl_3(L^2)]$), respectively.



Scheme 1.

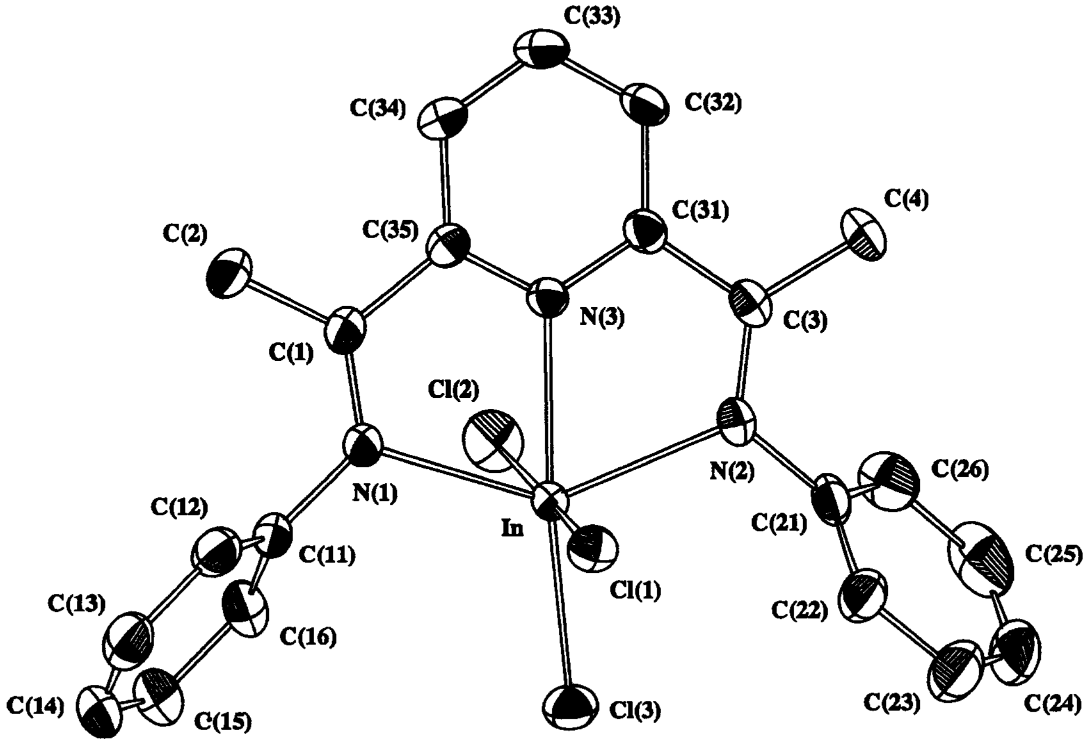


Fig. 2. Molecular structure of $[InCl_3(L^2)]$ along with the atomic numbering scheme.

Table 3. Selected bond lengths (Å) and angles (°) in $[InCl_3(L^2)] \cdot CH_3CN$

In—Cl(1)	2.466(1)	N(1)—C(1)	1.281(3)
In—Cl(2)	2.473(1)	N(2)—C(3)	1.289(3)
In—Cl(3)	2.401(1)	N(3)—C(31)	1.336(3)
In—N(1)	2.338(2)	N(3)—C(35)	1.331(3)
In—N(2)	2.307(2)	C(1)—C(35)	1.492(4)
In—N(3)	2.247(2)	C(3)—C(31)	1.488(4)
Cl(1)—In—Cl(2)	175.07(3)	N(3)—In—Cl(3)	173.39(6)
Cl(1)—In—Cl(3)	92.42(4)	N(3)—In—N(1)	70.67(8)
Cl(1)—In—N(2)	91.94(6)	N(3)—In—N(2)	70.87(8)
Cl(2)—In—Cl(3)	91.01(4)	C(11)—N(1)—In	120.5(2)
Cl(2)—In—N(2)	90.73(6)	C(21)—N(2)—In	120.2(2)
N(1)—In—Cl(1)	86.21(6)	N(1)—C(1)—C(35)	116.5(2)
N(1)—In—Cl(2)	89.12(6)	N(2)—C(3)—C(31)	116.6(2)
N(1)—In—Cl(3)	115.26(6)	N(3)—C(31)—C(3)	115.5(2)
N(1)—In—N(2)	141.46(8)	N(3)—C(35)—C(1)	116.2(2)
N(2)—In—Cl(3)	103.28(6)	C(1)—N(1)—In	117.5(2)
N(3)—In—Cl(1)	90.89(6)	C(3)—N(2)—In	118.0(2)
N(3)—In—Cl(2)	86.07(6)		

The methanol ligand in $[InCl_3(L^1)(MeOH)]$ can easily be replaced by other monodentate ligands, whereas for the substitution of chloro ligands powerful chelators are required. A summary of the performed reactions are given in Scheme 1. $[InCl_3(L^1)(OH_2)]$ is obtained when $[InCl_3(L^1)(MeOH)]$ is refluxed in acetone and water is added. The deposited crystals are only sparingly soluble in common organic solvents. Dissolution in hot methanol is followed by ligand exchange OH_2 *vs* MeOH. $[InCl_3(L^1)(OH_2)]$ has been characterized by IR spectroscopy and FAB^+ mass spectrometery, giving no unusual features. An X-ray structure determination confirms the molecular structure. The compound crystallizes in the triclinic space group $P\bar{1}$. Figure 3 shows an ORTEP [6] representation of the molecule along

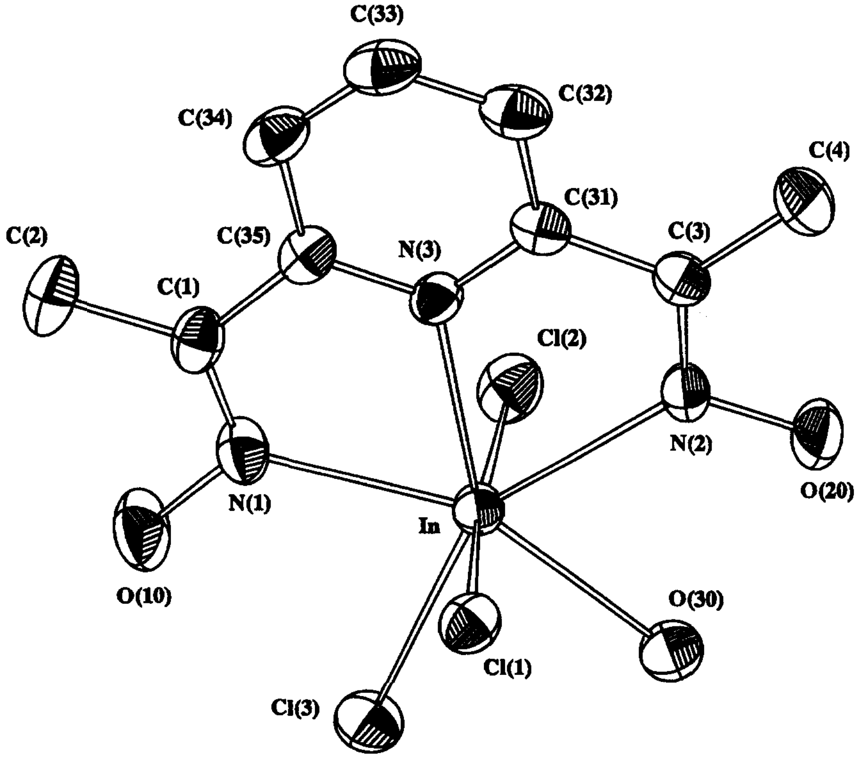


Fig. 3. Molecular structure of $[InCl_3(L^1)(OH_2)]$ along with the atomic numbering scheme.

Table 4. Selected bond lengths (Å) and angles (°) in $[InCl_3(L^1)(OH_2)]$

In—Cl(1)	2.434(1)	N(1)—O(10)	1.373(4)
In—Cl(2)	2.400(1)	N(1)—C(1)	1.272(4)
In—Cl(3)	2.591(1)	N(2)—O(20)	1.387(4)
In—N(1)	2.370(3)	N(2)—C(3)	1.277(4)
In—N(2)	2.421(3)	N(3)—C(31)	1.343(4)
In—N(3)	2.364(3)	N(3)—C(35)	1.341(4)
In—O(30)	2.370(3)	C(1)—C(35)	1.483(5)
		C(3)—C(31)	1.481(5)
Cl(1)—In—Cl(2)	174.17(3)	N(3)—In—Cl(2)	91.52(7)
Cl(1)—In—Cl(3)	90.87(4)	N(3)—In—Cl(3)	145.83(7)
Cl(1)—In—O(30)	86.2(1)	N(3)—In—O(30)	136.7(1)
Cl(1)—In—N(2)	88.65(8)	N(3)—In—N(1)	66.54(9)
Cl(2)—In—Cl(3)	93.38(4)	N(3)—In—N(2)	66.26(9)
Cl(2)—In—O(30)	90.9(1)	O(30)—In—Cl(3)	77.00(8)
Cl(2)—In—N(2)	85.62(8)	O(10)—N(1)—In	122.4(2)
N(1)—In—Cl(1)	91.96(8)	O(20)—N(2)—In	124.9(2)
N(1)—In—Cl(2)	92.73(8)	N(1)—C(1)—C(35)	113.9(3)
N(1)—In—Cl(3)	79.45(8)	N(2)—C(3)—C(31)	114.7(3)
N(1)—In—O(30)	156.3(1)	N(3)—C(31)—C(3)	116.5(3)
N(1)—In—N(2)	132.7(1)	N(3)—C(35)—C(1)	116.3(3)
N(2)—In—Cl(3)	147.84(7)	C(1)—N(1)—In	123.4(2)
N(2)—In—O(30)	70.9(1)	C(3)—N(2)—In	121.9(2)
N(3)—In—Cl(1)	87.19(7)		

with the atomic numbering scheme. Table 4 summarizes selected bond lengths and angles. The bonding situation in $[InCl_3(L^1)(OH_2)]$ is very similar to that in $[InCl_3(L^1)(MeOH)]$. The only significant difference is the In—O bond length which is shorter by 0.16 Å in the aqua complex.

The anionic $[InCl_4(L^1)]^-$ we have first isolated as a by-product which is formed in low yield during the reaction of $[InCl_3(L^1)(MeOH)]$ with sodium diethyldithiocarbamate, $NaEt_2dtc$. The major product of this reaction is the well known neutral tris-chelate $[In(Et_2dtc)_3]$, which immediately precipitates from the methanolic reaction solution. When the precipitation of the tris chelate was finished, a small amount (about 5 per cent of the overall yield) of colourless cubes crystallized, which could be characterized as $(Et_2NH_2)[InCl_4(L^1)]$. The molecular structure of the anion is given in Fig. 4. Table 5 contains the corresponding bond lengths and angles. The $(Et_2NH_2)^+$ cation results from the decomposition of Et_2dtc^-. Similar reactions have been obtained previously during the reaction of sodium diethyldithiocarbamate with metal complexes [7]. Another and more feasible approach to $[InCl_4(L^1)]^-$ is the reaction of $[InCl_3(L^1)(MeOH)]$ with dilute HCl in acetone. The complex anion can be isolated from this reaction as its tetrabutylammonium or tetraphenylphosphonium salt after addition of $(Bu_4N)Cl$ or $(Ph_4P)Cl$, respectively.

A structure determination was performed on a pale-brown needle of $(Et_2NH_2)[InCl_4(L^1)]$ which was obtained from the reaction of $[InCl_3(L^1)(MeOH)]$ with $NaEt_2dtc$. The compound crystallizes in the triclinic space group $P\bar{1}$. The general coordination feature of In^{III} is not significantly influenced by the replacement of MeOH by Cl^- and the formation of a complex anion.

The structure is characterized by a pentagonal bipyramidal coordination polyhedron with an almost planar equatorial plane (maximum deviation from the mean least square plane between the atoms N(1), N(2), N(3), Cl(3), Cl(4) and In: 0.082 Å). The bond lengths to the equatorially coordinated chloro ligands are markedly longer than those to the axial ligands. No unusual structural features have been observed for the $(Et_2NH_2)^+$ cation.

SUMMARY

It has been shown that indium(III) chloride reacts with the tridentate amine oxime L^1 and the structurally similar Schiff base ligand L^2 to form stable indium(III) complexes. The structure of the products are dependent on the steric requirements of the ligands. The more bulky ligand L^2 forms a distorted octahedral complex $[InCl_3(L^2)]$, whereas L^1 realizes seven coordination with indium(III) by the introduction of one molecule of MeOH from the solvent into the coordination sphere. The different coordination behaviour of the structurally similar ligands

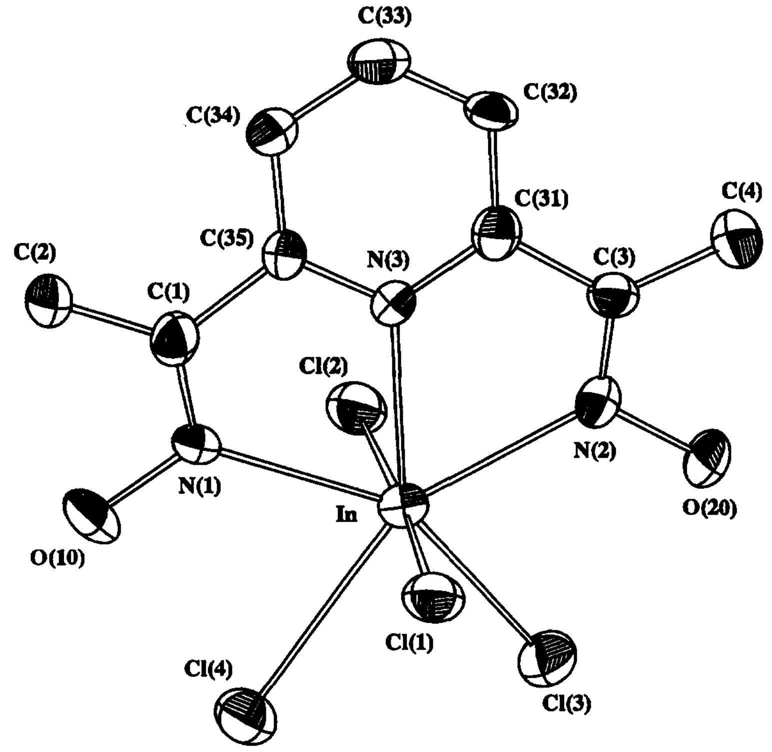


Fig. 4. Molecular structure of $[InCl_4(L^1)]^-$ along with the atomic numbering scheme.

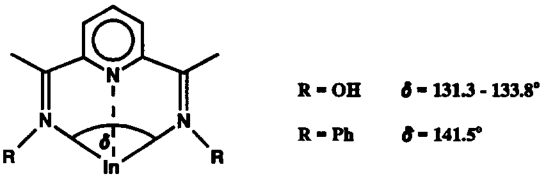
Table 5. Selected bond lengths (Å) and angles (°) in $(Et_2NH_2)[InCl_4(L^1)]$

In—Cl(1)	2.412(2)	N(1)—O(10)	1.383(9)
In—Cl(2)	2.418(2)	N(1)—C(1)	1.28(1)
In—Cl(3)	2.562(2)	N(2)—O(20)	1.380(9)
In—Cl(4)	2.892(2)	N(2)—C(3)	1.27(1)
In—N(1)	2.415(7)	N(3)—C(31)	1.35(1)
In—N(2)	2.386(7)	N(3)—C(35)	1.33(1)
In—N(3)	2.395(6)	C(1)—C(35)	1.49(1)
		C(3)—C(31)	1.47(1)

Cl(1)—In—Cl(2)	175.55(8)	N(3)—In—Cl(2)	89.8(2)
Cl(1)—In—Cl(3)	94.67(8)	N(3)—In—Cl(3)	144.0(2)
Cl(1)—In—Cl(4)	87.81(7)	N(3)—In—Cl(4)	140.3(2)
Cl(1)—In—N(2)	89.5(2)	N(3)—In—N(1)	65.8(2)
Cl(2)—In—Cl(3)	89.06(8)	N(3)—In—N(2)	65.6(2)
Cl(2)—In—Cl(4)	90.76(7)	Cl(4)—In—Cl(3)	75.67(7)
Cl(2)—In—N(2)	93.6(2)	O(10)—N(1)—In	123.9(5)
N(1)—In—Cl(1)	89.6(2)	O(20)—N(2)—In	122.0(5)
N(1)—In—Cl(2)	85.9(2)	N(1)—C(1)—C(35)	114.9(7)
N(1)—In—Cl(3)	149.9(2)	N(2)—C(3)—C(31)	114.4(7)
N(1)—In—Cl(4)	74.7(2)	N(3)—C(31)—C(3)	115.9(7)
N(1)—In—N(2)	131.3(2)	N(3)—C(35)—C(1)	115.9(7)
N(2)—In—Cl(3)	78.6(2)	C(1)—N(1)—In	122.6(5)
N(2)—In—Cl(4)	153.8(2)	C(3)—N(2)—In	124.2(5)
N(3)—In—Cl(1)	88.6(2)		

may be supported by the slightly different overall bite angles N(1)—In—N(2) (see Scheme 2) which obviously influence the ability of the metal to realize a planar, five-coordinate equatorial coordination plane.

The methanol ligand in $[InCl_3(L^1)(MeOH)]$ can easily be replaced by OH_2 or Cl^- to give structurally similar, pentagonal-bipyramidal indium(III) complexes. Further ongoing ligand exchange can be



Scheme 2.

achieved, when powerful chelating ligands are used. With sodium diethyldithiocarbamate the known tris-chelate $[InL_3]$ is obtained. Reactions of $[InCl_3(L^1)(MeOH)]$ with bidentate ligands and the structures of the products are reported elsewhere [8].

Acknowledgements—The work was financially supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. S.A. 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. Organometallic Chem.* 1980, **184,** 309.
2. Metzger, H. in Houben/Weyl, *Methoden der organischen Chemie*, vol. X/4, p. 58, Georg Thieme Verlag, Stuttgart (1968).
3. Dymock, K., Palenik, G. J., Slezak, J., Raston, C. L., White, A. H., *J. Chem. Soc., Dalton Trans.* 1976, 28.
4. Sheldrick, G. M., *SHELXS*86—*A Program for the Solution of X-Ray Structures*, University of Göttingen (1986).
5. Sheldrick, G. M., *SHELXL*93—*A Program for the Refinement of X-Ray Structures*, University of Göttingen (1993).
6. Zsolnai, L., *ZORTEP—A Program for the Ellipsoid Presentation of X-Ray Structure Results*, University of Heidelberg (1994).
7. Abram, U. and Lorenz, B., *Z. Naturforsch*, 1993, **48b,** 771.
8. Abram, S., Maichle-Mössmer, C. and Abram, U., *Polyhedron*, **16,** 2291.
9. Spek, A., *PLATON, HELENA—Programs for Data Reduction and Calculation on X-Ray Data*, University of Utrecht (1994).
10. Frenz, B. A., *Enraf-Nonius Structure Determination Package, SDP User's Guide*. Enraf-Nonius, Delft (1983).
11. Kretschmar, M., *HKL—A Program for the Conversion of X-Ray Data*, University of Tübingen (1993).