

The Structure of Trichlorobis(trimethylamine)indium(III)

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Abstract. $[\text{InCl}_3(\text{C}_3\text{H}_9\text{N})_2]$, $M_r = 339.3$, orthorhombic, $Pnmb$, $a = 10.09$ (1), $b = 9.99$ (1), $c = 13.08$ (1) Å, $U = 1318.7$ Å³, $Z = 4$, $D_x = 1.71$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 23.4$ cm⁻¹, $F(000) = 672$, room temperature, final $R = 0.067$, $wR = 0.069$ for 639 independent observed reflections. In the discrete $\text{InCl}_3(\text{NMe}_3)_2$ molecule, which has imposed C_s symmetry, the indium atom has a five-coordinate undistorted trigonal bipyramidal environment, being bonded to three chlorine atoms [$\text{In}-\text{Cl}$ 2.376 (4), 2.343 (8) Å] in the equatorial plane and two trimethylamine ligands in axial positions [$\text{In}-\text{N}$ 2.345 (19), 2.320 (20) Å].

Introduction. For the neutral species $\text{In}X_3L_2$ ($X =$ halogen, $L =$ monodentate N, O, P, S donor ligand) a five-coordinate geometry based on a *trans* trigonal bipyramid (t.b.p.) structure (D_{3h}) is usual (Carty & Tuck, 1975). In the majority of cases, confirmation is provided by spectroscopic (IR and Raman) data; in only one instance, *i.e.* $\text{InCl}_3(\text{PPh}_3)_2$, has a complete X-ray structure determination been reported (Veidis & Palenik, 1969). Surprisingly, $\text{InI}_3(\text{Me}_2\text{SO})_2$ does not belong to this pentacoordinate classification; the structure is ionic and comprises octahedral $[\text{InI}_2(\text{Me}_2\text{SO})_4]^+$ cations and tetrahedral $[\text{InI}_4]^-$ anions (Einstein & Tuck, 1970).

For the trimethylamine complexes ($X = \text{Cl}, \text{Br}, \text{I}$, $L = \text{NMe}_3$) in particular, spectroscopic characterization is complete and without controversy apart from $\text{InI}_3(\text{NMe}_3)_2$ where the identity of the molecular species is in question (Beattie, Gilson & Ozin, 1969; Beattie & Ozin, 1969). Previous IR and Raman spectroscopic data for $\text{InCl}_3(\text{NMe}_3)_2$ indicate that the t.b.p. structure persists in solution. Our proton NMR (¹H) evidence is equally clear-cut. The sharp singlet associated with equivalent methyl-group protons observed in the room-temperature (298 K) ¹H NMR spectrum (90 MHz, CDCl_3) at δ_{CH_3} 2.54 is retained with no discernible change over the temperature range 320–218 K.

Experimental. Title compound prepared by direct treatment of anhydrous metal halide with excess trimethylamine as previously described (Beattie, Gilson & Ozin, 1969). An alternative and much faster route to

same product involved reaction of excess amine with solution of InCl_3 in tetrahydrofuran. Recrystallization from benzene solution gave colourless needle-shaped crystals, m.p. 467–469 K (decomposition), extremely air-moisture sensitive. Crystal $0.3 \times 0.3 \times 0.3$ mm loaded in capillary under nitrogen. Density could not be measured. Space group $Pnmb$ (No. 62, transformation $a \rightarrow b$, $b \rightarrow a$) from systematic absences $h0l$, $h+l = 2n+1$, $hk0$, $k = 2n+1$ and from successful structure determination. Precession photographs established preliminary cell constants. Crystal then mounted on Stoe STADI2 diffractometer to rotate about a axis. Cell dimensions obtained by measurement of ca 20 high-angle axial reflections, $\theta_{\text{max}} = 25^\circ$. Intensity data collected *via* variable-width ω scan, background counts 20 s, step-scan rate 0.033°s^{-1} applied to width of $(1.5 + \sin\mu/\tan\theta)$. Empirical absorption correction applied (Walker & Stuart, 1983); absorption corrections 0.7–1.5. Standard reflections $h22$ measured every 20 measurements for each layer; intensities dropped by ca 30% and linear correction applied. 1321 ($0 \leq h < 11$, $0 \leq k < 11$, $0 \leq l < 15$) data measured with $2\theta_{\text{max}} 50^\circ$. 639 data with $I > 3\sigma(I)$ used in subsequent calculations. Structure solved *via* usual heavy-atom methods. In, N, C atoms refined anisotropically; H atoms bonded to C and N placed in tetrahedral positions and refined with geometric constraints. Thermal parameters of H allowed to refine but those on same atom constrained to be equivalent. Weighting scheme $w = 1/[\sigma^2(F) + 0.003F^2]$, $\sigma(F)$ from counting statistics. Scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations using *SHELX76* (Sheldrick, 1976) and some of our own programs on the Amdahl V7A at the University of Reading. In final cycle of refinement no shift $> 0.1\sigma$. In final difference Fourier map, max. and min. peak heights 1.2 and -0.8 e \AA^{-3} . Atomic coordinates are given in Table 1 and details of interatomic distances and angles in Table 2.*

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42727 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The structure is made up of discrete molecules of $\text{InCl}_3(\text{NMe}_3)_2$, with crystallographically imposed C_s symmetry. The molecule is shown in Fig. 1 together with the atomic numbering scheme. There are no significant deviations from ideal trigonal bipyramidal geometry with mean distances of In—Cl (equatorial) 2.365 (11) Å and In—N (axial) 2.332 (25) Å.

Table 1. Atomic coordinates ($\times 10^4$) with e.s.d.'s in parentheses

$$\bar{U}_{\text{eq}} = \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$\bar{U}_{\text{eq}} (\text{Å}^2 \times 10^3)$
In	2500	2991 (2)	248 (1)	90 (1)
Cl(1)	4512 (4)	2193 (5)	967 (4)	109 (5)
Cl(2)	2500	4494 (10)	-1127 (6)	132 (6)
N(1)	2500	1170 (20)	-883 (15)	90 (17)
N(2)	2500	4795 (20)	1364 (15)	94 (16)
C(1)	1261 (21)	5661 (24)	1180 (19)	129 (28)
C(2)	2500	4372 (37)	2401 (20)	113 (27)
C(3)	1324 (23)	1265 (23)	-1527 (15)	115 (28)
C(4)	2500	-99 (29)	-351 (24)	122 (29)

Table 2. Molecular dimensions; distance in Å, angles in degrees

In—Cl(1)	2.376 (4)	N(1)—C(3)	1.459 (25)
In—Cl(2)	2.343 (8)	N(1)—C(4)	1.447 (36)
In—N(1)	2.345 (19)	N(2)—C(1)	1.540 (26)
In—N(2)	2.320 (20)	N(2)—C(2)	1.420 (33)
Cl(1)—In—Cl(2)	121.27 (14)	In—N(1)—C(3)	108.3 (12)
Cl(1)—In—N(1)	89.39 (32)	In—N(1)—C(4)	112.1 (15)
Cl(2)—In—N(1)	90.8 (6)	C(3)—N(1)—C(4)	109.6 (14)
Cl(1)—In—N(2)	90.66 (29)	C(3)—N(1)—C(3')	108.9 (17)
Cl(2)—In—N(2)	89.1 (5)	In—N(2)—C(1)	109.8 (11)
N(1)—In—N(2)	179.90 (13)	In—N(2)—C(2)	111.7 (18)
Cl(1)—In—Cl(1')	117.45 (19)	C(1)—N(2)—C(2)	108.5 (14)
		C(1)—N(2)—C(1')	108.6 (17)

Symmetry code: (i) 0.5-x, y, z.

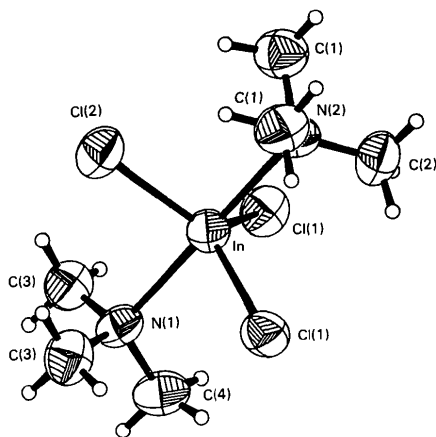


Fig. 1. The $\text{InCl}_3(\text{NMe}_3)_2$ molecule. Thermal ellipsoids are shown at the 50% probability level.

The structure is isomorphous with a number of other $\text{MX}_3(\text{NMe}_3)_2$ molecules including $M = \text{Ti}$, $X = \text{Br}$ (Greene, Russ & Wood, 1971), V , Cl (Greene & Orioli, 1969), Cr , Cl (Greene, Russ & Wood, 1971), Fe , Cl (Millington, Wade, Willey & Drew, 1984). In these structures the difference between $M\text{—Cl}$ and $M\text{—N}$ varies considerably. For vanadium and chromium the $M\text{—Cl}$ bond is longer by 0.04, 0.09 Å, while in the iron complex the $M\text{—Cl}$ bond is shorter by 0.05 Å. In the present structure the mean In—Cl bond length is greater by 0.032 Å.

The In—Cl bonds can be viewed as single bonds and compare favourably with mean values of 2.383 Å in $\text{InCl}_3(\text{PPh}_3)_2$ (Veidis & Palenik, 1969), 2.448 Å in $(\text{Et}_4\text{N})_2(\text{InCl}_6)^{2-}$ (Brown, Einstein & Tuck, 1969), 2.45 Å in $[\text{InCl}_4(\text{H}_2\text{O})_2]^-$ (Zeigler, Schlimper, Nuber, Weiss & Ertl, 1975) and 2.39 Å in $[\text{MeInCl}_2]$ (Hausen, Mertz, Veigel & Weidlein, 1974). Carty & Tuck (1975) propose a value of 2.30 Å for a single In—Cl bond length but this seems an underestimate.

There are no direct comparisons of In—NMe₃ distances but mention can be made of $\text{InCl}(\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_2$ (Khan, Steevensz, Tuck, Noltes & Corfield, 1980) in which the two nitrogen atoms occupy axial positions at distances of 2.44, 2.48 Å from the metal. These bonds may be lengthened in comparison with the present structure by chelate steric effects. There are several structures in the Cambridge Data Centre files which include an In—N(sp^2) bond with a range of distances from 2.27 to 2.52 Å but there are insufficient of these for any definite conclusions to be drawn.

It is interesting to compare the present structure with that of $\text{InCl}_3(\text{PPh}_3)_2$ (Veidis & Palenik, 1969) which is also a trigonal bipyramid with mean In—Cl 2.383 and In—P 2.712 Å. The similarity in In—Cl distances is also reflected in the solid-state IR metal-halogen stretching frequencies [$\nu(\text{In—Cl})$, $\text{InCl}_3(\text{NMe}_3)_2$ 323, $\text{InCl}_3(\text{PPh}_3)_2$ 319 cm^{-1}]. However, there is clearly a very significant difference in bond strength between In—N (mean 2.332 Å) and In—P (mean 2.712 Å). It is difficult to differentiate unequivocally between the two ligands in terms of steric factors. Both can be regarded as bulky ligands (Zakrobsky, 1971) but there must be a subtle imbalance in the steric influence between and exerted by the phenyl groups of the phosphine and the methyl groups of the amine which affects bond formation of In—N vs In—P (Carty & Tuck, 1975). Some indication of the steric bulk of the tertiary phosphine is provided by the cone-angle approach of Tolman (1970) which gives PPh_3 (145°) and for comparison PMe_3 (118°). From the standpoint of electronic influence, certainly the 'hard' acceptor character of In^{III} would be more sympathetic to the amine than to the phosphine based on $\text{N} > \text{P}$ for class (a) donors and would be compatible with the observed binding order In—N > In—P. The point in question is whether the difference between them

is significant. The bonding model suggested by Carty & Tuck (1975) for $\text{InCl}_3(\text{PPh}_3)_2$ uses $\text{In}(sp^2)$ to bind the equatorial halogen atoms with the empty orthogonal p_z orbital as σ acceptor for the axial phosphines. From covalent radii, they estimate the In—P distances (mean 2.71 Å) to be at least 0.2 Å longer than expected for a single bond and conclude that there is little evidence of $5d$ orbital involvement in either a σ or a π sense. Carty & Tuck also estimate In—N single-bond lengths to be in the range 2.20–2.40 Å as indeed are the values in the present structure. Shortening of the In—N bonds relative to In—P bonds could be accounted for by the inclusion of a small d_{z^2} orbital σ contribution in conjunction with the much smaller nitrogen atom.

There are no contacts less than van der Waals radii between molecules.

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Structure du Bis(*N,N*-dibutylodécaneamide)dinitratodioxouranium(VI)

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Abstract. $[\text{UO}_2(\text{NO}_3)_2(\text{C}_{20}\text{H}_{41}\text{NO})]$, $M_r = 1017.15$, monoclinic, $P2_1/c$, $a = 27.604$ (2), $b = 9.843$ (3), $c = 19.166$ (2) Å, $\beta = 100.21$ (8)°, $V = 5124.7$ Å³, $Z = 4$, $D_x = 1.318$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 30.50$ cm⁻¹, $F(000) = 2088$, room temperature, $R_F = 0.053$ for 2211 unique observed reflections. The coordination polyhedron of the U atom is a bipyramid with a hexagonal base made up of six oxygen atoms which belong to two bidentate nitrates [U—O 2.51 (2) (×2), 2.53 (2) Å (×2)] and two monodentate *N,N*-dibutylodécaneamides [U—O 2.36 (1), 2.39 (2) Å]. In the apical positions are the two oxygens of the uranyl group [U—O 1.71 (1), 1.74 (1) Å]. Both *n*-butyl and undecyl chains of the amide are in a *trans* conformation. The two extended undecyl chains, which lie perpendicular to the hexagonal equatorial plane on the same side, are parallel to the UO_2^{2+} linear ion. The

packing of the molecules is such that the butyl and the undecyl chains are located in distinct regions of the cell.

Introduction. Le nitrate de dioxouranium(VI) forme avec les amides des complexes de type $\text{UO}_2(\text{NO}_3)_2L_2$, L

étant un amide *N,N* substitué de type $R1\text{CON} \begin{matrix} R2 \\ \diagdown \\ R3 \end{matrix}$. En

utilisant des amides aliphatiques dans lesquels $R1$, $R2$ ou $R3$ peuvent être ramifiés ou linéaires, un grand nombre de composés ont été préparés et caractérisés par spectroscopie IR (Bagnall & Vélasquez Lopez, 1975; Bagnall, Vélasquez Lopez & Brown, 1976): les amides sont tous coordonnés à l'uranyle par l'oxygène du groupe CO, les nitrates bidentés complétant l'hexagone dans le plan équatorial de l'uranyle. Cependant, peu de structures cristallines sont connues: celle de $\text{UO}_2(\text{NO}_3)_2$ -