

Trichloro(2,6-di-2-pyridylpyridine- κ^3N)-indium(III)

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Key indicators

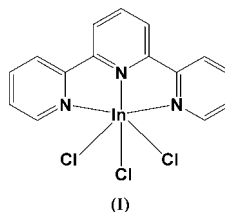
Single-crystal X-ray study
T = 103 K
Mean σ (C–C) = 0.003 Å
R factor = 0.023
wR factor = 0.058
Data-to-parameter ratio = 19.8

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title complex, [InCl₃(C₁₅H₁₁N₃)], the mutually *trans* bond lengths In–N [2.2438 (16) Å] and In–Cl [2.4080 (5) Å] are shorter than the other In–N and In–Cl bonds (each *trans* to their own kind). This *trans* influence was observed earlier in *d*¹⁰ metal complexes of 2,6-di-2-pyridylpyridine. The crystal structure of (I) is stabilized by extensive intermolecular C–H···Cl hydrogen bonding.

Comment

The structures of five metal complexes of 2,6-di-2-pyridylpyridine (tpy) with stoichiometry *M*(tpy)Cl₃ have been previously reported for *M* = Ga (Beran *et al.*, 1970), *M* = In, Tl (Palenik & Dymock, 1974), *M* = Ru (Laurent *et al.*, 1999) and *M* = Os (Demadis *et al.*, 1999).



In the case of *M* = In [Palenik & Dymock, 1974; Cambridge Structural Database (CSD; Allen, 2002) refcode TERPTL], only the cell parameters are available. It has been noted in the above structures that there is a significant *trans* influence observed in both the *M*–N and *M*–Cl bond lengths. This is manifested in differences between the mutually *trans* *M*–N and *M*–Cl bond length compared to the other *M*–N and *M*–Cl bond lengths. This effect appears to be different in *d*⁵ metal complexes compared to *d*¹⁰ complexes. Prior to the present structure determination, there was only one such example of the latter type of complex, namely Ga(tpy)Cl₃ (Beran *et al.*, 1970). In this structure, the mutually *trans* Ga–N and Ga–Cl distances are 2.034 (7) and 2.235 (8) Å, respectively. The remaining two Ga–N and two Ga–Cl distances are 2.110 (6)/2.115(6) and 2.329 (3)/2.403(2) Å, respectively. Thus, in this instance, the *trans* influence is manifested by a shortening of the Ga–N and Ga–Cl bonds compared to the non-*trans* bonds. This is contrasted with the *trans* influence observed in *M*(tpy)Cl₃ complexes of *d*¹⁰ metals, such as Os^{III} (Demadis *et al.*, 1999) and Ru^{III} (Laurent *et al.*, 1999). In these complexes, there is a similar shortening of the *M*–N distances [Os–N_{*trans*} = 1.969 (3) Å compared to 2.075 (3) and 2.077 (3) Å; Ru–N_{*trans*} = 2.061 (6) Å compared to 2.060 (8) and 2.093 (7) Å]. However, the *trans* influence in the *M*–Cl distances in these *d*⁵ metal complexes is in the opposite sense to that observed in *d*¹⁰ metal complexes. In these complexes, the *trans* (to *M*–N)

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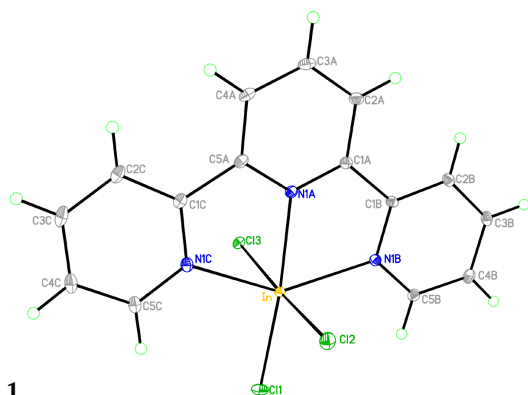


Figure 1
View of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 20% probability level.

M –Cl bond lengths are longer [Ru–Cl_{trans} = 2.468 (2) Å and Os–Cl_{trans} = 2.3833 (9) Å] than the non-*trans* M –Cl bonds [Ru–Cl = 2.402 (2) and 2.424 (2) Å; Os–Cl = 2.360 (1) and 2.3741 (8) Å].

The title compound, In(tpy)Cl₃ (I), is only the second d^{10} metal complex of tpy with an M (tpy)Cl₃ stoichiometry to be structurally characterized. In this structure, the In metal center has a pseudo-octahedral configuration with the three N atoms of the tpy ligand coordinated in a meridional fashion, with the others three positions in the coordination sphere occupied by the Cl ligands. The *cis*-Cl–In–Cl angles (Table 1) differ by less than 4°, while the *cis*-N–In–N angles differ by more than 17° from the ideal value of 90° for an octahedron, as a result of the constraints imposed by the tpy ligand. Further evidence of this distortion can be seen in the *trans* N–In–N and Cl–In–Cl bond angles [144.73 (6) and 176.11 (2)°]. The *trans* influence observed in In(tpy)Cl₃ is similar to that found in Ga(tpy)Cl₃. The mutually *trans* In–N and In–Cl bond lengths are shorter than the other In–N and In–Cl bonds [2.244 (2) *versus* 2.270 (2) and 2.277 (2) Å for In–N, and 2.4080 (5) *versus* 2.4735 (6) and 2.5155 (5) Å for In–Cl]. There is extensive intermolecular hydrogen bonding between the three Cl ligands and some of the H atoms of the tpy ligand (Table 2 and Fig. 2).

Experimental

In (0.0224 g), S (0.0193 g), ZnCl₂ (0.0130 g), 2,6-di-2-pyridylpyridine (0.009 g) and AuCl₃ (0.312 g) were mixed in a 3 mm ID/5 mm OD quartz tube with 50/50 ethylene glycol–water. The tube was sealed at a height of 15.5 cm (fill = 65%). The tube was counter-pressurized and heated in a Leco hydrothermal system to a hot-zone temperature of 466 K for 92 h. At the bottom of the tube was a mass of colorless crystals along with orange and black powders.

Crystal data

[InCl₃(C₁₅H₁₁N₃)]
 M_r = 454.44
 Monoclinic, $P2_1/n$
 a = 8.4662 (6) Å
 b = 14.1130 (9) Å
 c = 14.1329 (10) Å
 β = 106.2530 (10)°
 V = 1621.16 (19) Å³
 Z = 4

D_x = 1.862 Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 5463 reflections
 θ = 5.1–56.6°
 μ = 1.95 mm⁻¹
 T = 103 (2) K
 Triangular prism, pale yellow
 0.40 × 0.35 × 0.15 mm

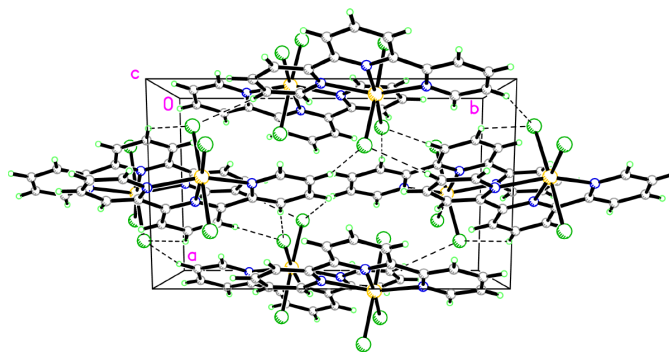


Figure 2
The molecular packing of (I), viewed down the c axis.

Data collection

Bruker SMART CCD area-detector diffractometer	3965 independent reflections
φ and ω scans	3696 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1999)	$R_{int} = 0.040$
$T_{min} = 0.568$, $T_{max} = 0.746$	$\theta_{max} = 28.3^\circ$
12733 measured reflections	$h = -10 \rightarrow 11$
	$k = -18 \rightarrow 18$
	$l = -17 \rightarrow 18$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0247P)^2 + 1.37P]$
$R[F^2 > 2\sigma(F^2)] = 0.024$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.058$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.09$	$\Delta\rho_{max} = 0.42 \text{ e \AA}^{-3}$
3965 reflections	$\Delta\rho_{min} = -0.38 \text{ e \AA}^{-3}$
200 parameters	Extinction correction: <i>SHELXTL</i>
H-atom parameters constrained	Extinction coefficient: 0.0014 (3)

Table 1

Selected geometric parameters (Å, °).

In–N1A	2.2438 (16)	In–Cl1	2.4080 (5)
In–N1C	2.2697 (17)	In–Cl2	2.4735 (6)
In–N1B	2.2769 (17)	In–Cl3	2.5155 (5)
N1A–In–N1C	72.38 (6)	N1B–In–Cl2	88.15 (5)
N1A–In–N1B	72.41 (6)	Cl1–In–Cl2	93.21 (2)
N1C–In–N1B	144.73 (6)	N1A–In–Cl3	84.03 (4)
N1A–In–Cl1	174.05 (5)	N1C–In–Cl3	87.27 (5)
N1C–In–Cl1	104.84 (5)	N1B–In–Cl3	91.13 (4)
N1B–In–Cl1	110.41 (4)	Cl1–In–Cl3	90.629 (19)
N1A–In–Cl2	92.11 (4)	Cl2–In–Cl3	176.109 (18)
N1C–In–Cl2	91.11 (5)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2A–H2AA \cdots Cl1 ⁱ	0.95	2.71	3.664 (2)	178
C2B–H2BA \cdots Cl1 ⁱ	0.95	2.69	3.634 (2)	174
C2C–H2CA \cdots Cl2 ⁱⁱ	0.95	2.83	3.625 (2)	142
C3A–H3AA \cdots Cl3 ⁱⁱⁱ	0.95	2.74	3.484 (2)	136
C4B–H4BA \cdots Cl3 ^{iv}	0.95	2.76	3.613 (2)	149
C4C–H4CA \cdots Cl3 ^v	0.95	2.75	3.432 (2)	129

Symmetry codes: (i) $x - \frac{1}{2}, \frac{3}{2} - y, \frac{1}{2} + z$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $1 - x, 2 - y, 1 - z$; (iv) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (v) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

All H atoms were fixed in calculated positions with C–H = 0.95 Å and with isotropic displacement parameters fixed at 1.2 times that of the atom to which they were attached.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001; Sheldrick, 1999); program(s)

used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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