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Monochloroindium Derivative of tmtaa (Dibenzotetramethyltetraaza[14]annulene), $[In(C_{22}H_{22}N_4)Cl]$

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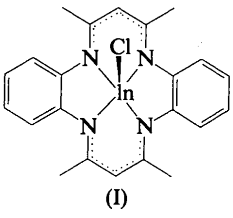
Abstract

The structure consists of an InCl fragment bonded symmetrically to the four N atoms of the macrocyclic ligand tmtaa (chloro{3,5,14,16-tetramethyl-2,6,13,17-tetraazatricyclo[16.4.0.$0^{7,12}$]docosa-1(18),2,5,7(12),8,10,13,16,-19,21-decaenediido-*N*,*N'*,*N''*,*N'''*}indium). This is the first structural characterization of an In entity coordinated to this ligand and reveals an unusual five-coordinate square-pyramidal geometry around the In atom. The metal is displaced 0.738 (3) Å above the N_4 coordination plane. The average In—N bond distance is 2.165 (5) Å and the In—Cl distance is 2.380 (2) Å.

Comment

The aim of this investigation was to confirm the expected *mm* symmetry, determine the displacement of the metal ion from the mean plane of the four N atoms of the macrocycle and compare the structure with similar derivatives of this ligand and other porphyrin systems. The molecular structure of the title compound, (I), and atomic labelling scheme are shown in Figs. 1 and 2.



(I)

Fig. 2 shows that the familiar saddle shape, adopted by the free macrocycle and arising from steric interactions between the methyl and phenyl groups, is retained in the metal complex (*cf.* Cotton & Czuchajowska, 1990). The metal is symmetrically bound 0.738 (3) Å above the N_4 plane. This displacement is significantly greater than that found for the Ga derivative (0.48 Å) (Atwood, Atwood, Cowley, Atwood & Román, 1992) and may be explained in terms of the larger covalent radius of In (1.41 Å) with respect to Ga (1.20 Å) (Alcock, 1990). The displacement of In from the N_4 plane is not unexpected, since the nitrogen-to-centre (N—Ct) distance of the dianionic tmtaa ligand lies in the range 1.85-1.87 Å (Weiss, Bursten, Peng & Goedkin, 1976), *i.e.* substantially less than the observed In—N distance [2.165 (5) Å]. As a result of metal coordination, torsional distortions and angle deformations occur in the 14-membered ring to minimize steric interactions, and the N—Ct distance increases to 2.035 Å.

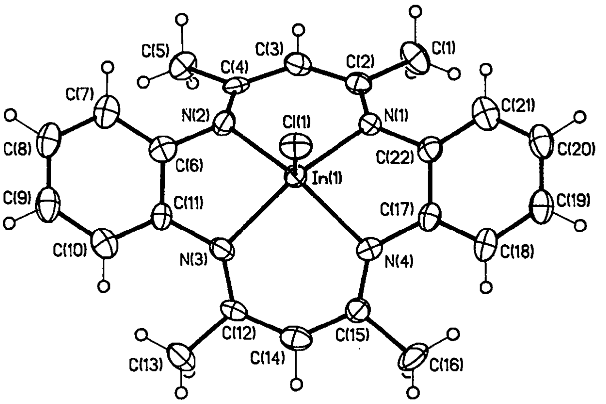


Fig. 1. Face view of [In(tmtaa)Cl] showing the atomic numbering scheme with displacement ellipsoids at 50% probability.

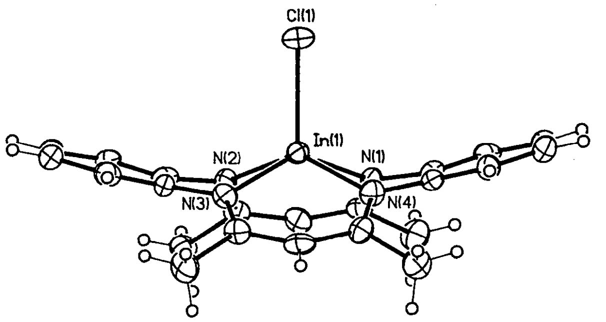


Fig. 2. Side view of [In(tmtaa)Cl] showing the saddle conformation adopted by the ligand.

The bond distances for In—Cl [2.380 (2) Å] and In—N [2.165 (5) Å average] are similar to those found in the related structure of tetraphenylporphyrinindium(III) chloride [2.369 (2) and 2.156 (6) Å average, respectively (Ball, Lee, Marshall & Trotter, 1980)]. It has been suggested that the metal-to-axial-group bond distance becomes greater as the charge donation to the metal from the macrocyclic ligand increases (Weiss, Bursten, Peng & Goedkin, 1976). Such charge donation is expected to be significantly larger for the $C_{22}H_{22}N_4^{2-}$ ligand compared

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to the delocalized porphyrin ligand. However, this effect is offset by the In atom being displaced only 0.61 Å from the porphyrin N_4 plane, as a result of the larger core size of this ligand (N—Ct = 2.067 Å). This results in relatively more charge donation from the porphyrin ligand leading to a balancing effect and an approximate equivalence in the metal-to-axial-atom distances.

On formation of the complex, the structure of the delocalized framework of the macrocycle is moderately affected. The average benzenoid C—N distance is 1.417 (5) Å, compared to 1.404 (8) Å for the free ligand (Goedkin, Pluth, Peng & Bursten, 1976). The C—C and C—N bond lengths of the 2,4-pentanediiminato unit indicate charge delocalization throughout the two six-membered chelate rings. The average C—N—C angle in the complex is 126.80°, compared to 125° for the unsaturated N atoms and 129° for the H(N) atoms in the free macrocycle.

Experimental

Reaction of anhydrous indium(III) chloride (1.25 g, 3.51 mmol) with $Li_2(C_{22}H_{22}N_4)$ (0.78 g, 3.52 mmol) in toluene at 343 K resulted in the formation of $[In(C_{22}H_{22}N_4)Cl]$ and two equivalents of LiCl. The complex was isolated as dark orange crystals by recrystallization from chloroform/hexane (20/80) solution.

Crystal data

$[In(C_{22}H_{22}N_4)Cl]$
$M_r = 492.71$
Monoclinic
$P2_1/c$
$a = 8.927$ (4) Å
$b = 22.457$ (7) Å
$c = 10.209$ (3) Å
$\beta = 101.34$ (3)°
$V = 2006.7$ (12) Å^3
$Z = 4$
$D_x = 1.631$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 16 reflections
$\theta = 8$-$9°$
$\mu = 1.33$ mm^{-1}
$T = 220$ (2) K
Blocks
0.51 × 0.15 × 0.11 mm
Dark orange

Data collection

Siemens *R*3*m* diffractometer
ω-2θ scans
Absorption correction: analytical
$T_{min} = 0.81$, $T_{max} = 0.86$
3700 measured reflections
3472 independent reflections
2672 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.0417$
$\theta_{max} = 25.00°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 26$
$l = -12 \rightarrow 11$
3 standard reflections monitored every 200 reflections
intensity variation: 8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0464$
$wR(F^2) = 0.1457$
$S = 1.059$
3457 reflections
266 parameters
H-atom parameters fixed

$\Delta\rho_{max} = 0.86$ e Å^{-3}
$\Delta\rho_{min} = -1.45$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1994)
Extinction coefficient: 0.0023 (6)

Calculated weights
$w = 1/[\sigma^2(F_o^2) + (0.0700P)^2 + 6.3000P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.025$

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
In(1)	0.17816 (5)	0.13459 (2)	0.49556 (4)	0.0234 (2)
Cl(1)	0.2860 (2)	0.08821 (8)	0.3261 (2)	0.0346 (4)
N(1)	0.0953 (6)	0.2230 (2)	0.4318 (5)	0.0261 (12)
N(2)	0.3501 (6)	0.1745 (2)	0.6493 (5)	0.0266 (12)
N(3)	0.1890 (6)	0.0744 (2)	0.6629 (5)	0.0255 (12)
N(4)	−0.0664 (6)	0.1233 (2)	0.4426 (5)	0.0295 (13)
C(1)	0.0657 (9)	0.3319 (3)	0.4564 (8)	0.039 (2)
C(2)	0.1472 (7)	0.2738 (3)	0.4961 (6)	0.0276 (14)
C(3)	0.2706 (8)	0.2763 (3)	0.6040 (6)	0.0293 (15)
C(4)	0.3559 (7)	0.2321 (3)	0.6814 (6)	0.0251 (14)
C(5)	0.4506 (8)	0.2528 (3)	0.8128 (6)	0.031 (2)
C(6)	0.4256 (8)	0.1279 (3)	0.7298 (6)	0.0280 (14)
C(7)	0.5819 (8)	0.1291 (3)	0.7879 (6)	0.033 (2)
C(8)	0.6525 (8)	0.0803 (3)	0.8559 (6)	0.038 (2)
C(9)	0.5710 (8)	0.0281 (3)	0.8621 (7)	0.038 (2)
C(10)	0.4167 (8)	0.0250 (3)	0.8022 (6)	0.034 (2)
C(11)	0.3405 (7)	0.0751 (3)	0.7369 (6)	0.0261 (14)
C(12)	0.0678 (8)	0.0476 (3)	0.6950 (6)	0.0265 (14)
C(13)	0.0806 (9)	0.0111 (3)	0.8205 (7)	0.039 (2)
C(14)	−0.0823 (8)	0.0530 (3)	0.6198 (7)	0.034 (2)
C(15)	−0.1476 (7)	0.0887 (3)	0.5104 (6)	0.0289 (15)
C(16)	−0.3211 (8)	0.0889 (4)	0.4772 (7)	0.041 (2)
C(17)	−0.1240 (7)	0.1626 (3)	0.3361 (6)	0.0267 (14)
C(18)	−0.2460 (8)	0.1506 (3)	0.2322 (6)	0.033 (2)
C(19)	−0.2858 (8)	0.1911 (3)	0.1280 (7)	0.037 (2)
C(20)	−0.2034 (8)	0.2426 (3)	0.1218 (7)	0.037 (2)
C(21)	−0.0775 (8)	0.2544 (3)	0.2220 (6)	0.034 (2)
C(22)	−0.0369 (7)	0.2167 (3)	0.3297 (6)	0.0271 (14)

Table 2. *Selected geometric parameters* (Å, °)

In(1)—N(4)	2.158 (5)	N(2)—C(4)	1.331 (8)
In(1)—N(2)	2.163 (5)	N(2)—C(6)	1.417 (8)
In(1)—N(3)	2.166 (5)	N(3)—C(12)	1.333 (8)
In(1)—N(1)	2.172 (5)	N(3)—C(11)	1.414 (8)
In(1)—Cl(1)	2.380 (2)	N(4)—C(15)	1.344 (8)
N(1)—C(2)	1.353 (8)	N(4)—C(17)	1.416 (8)
N(1)—C(22)	1.420 (8)		
N(4)—In(1)—N(2)	140.3 (2)	N(3)—In(1)—N(1)	140.0 (2)
N(4)—In(1)—N(3)	90.6 (2)	N(4)—In(1)—Cl(1)	107.49 (15)
N(2)—In(1)—N(3)	76.8 (2)	N(2)—In(1)—Cl(1)	112.2 (2)
N(4)—In(1)—N(1)	76.4 (2)	N(3)—In(1)—Cl(1)	109.80 (14)
N(2)—In(1)—N(1)	89.4 (2)	N(1)—In(1)—Cl(1)	110.16 (15)

The data were collected with the crystal mounted in a Lindemann tube, held at 220 K with an Oxford Cryosystem Cryostream Cooler (Cosier & Glazer, 1986). Data collection and cell refinement: Siemens *R*3*m* system. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1994).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: AB1129). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Hexakis(difluorphenylphosphan)-wolfram(0) hydrat, $W(PF_2Ph)_6.H_2O$

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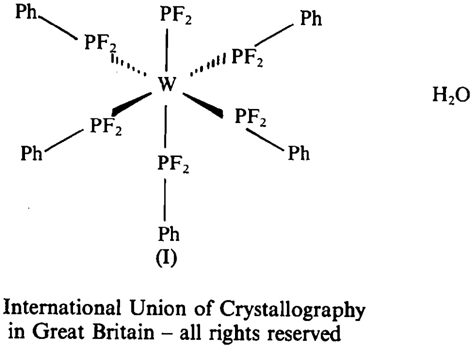
Abstract

The structure of a neutral complex of zero-valent tungsten, hexakis[difluoro(phenyl)phosphine]tungsten monohydrate, $[W(PF_2Ph)_6].H_2O$, is described. In comparison with the known structure of the analogous complex $[W(PF_2{}^tBu)_6]$ the title complex has a rather small W—P distance, indicating a stronger π-acceptor property of the PF_2Ph ligand.

Kommentar

Die Kristallstruktur enthält isolierte neutrale Komplexe $W(PF_2Ph)_6$ (I) (Fig. 1). Das zentrale Wolframatom besetzt eine Lage der Punktsymmetrie 32 und ist verzerrt oktaedrisch von den Liganden PF_2Ph umgeben. Die Phenylgruppen sind dabei mit ihren Ebenen parallel zur dreizähligen Achse ausgerichtet. Die Verzerrung von der idealen Oktaedersymmetrie, die in stärkerem Maße im $W(PF_2{}^tBu)_6$ (Krampe, Kruck & Tebbe, 1989) beobachtet wird, kann im $W(PF_2Ph)_6$ auf die Wechselwirkung der sperrigen Phenylgruppen und die damit verbundene Aufweitung der entsprechenden Winkel $\varphi(P—W—P) = 93{,}21\,(9)°$ zurückgeführt werden. Gleichzeitig wird eine mit $\varphi(P—W—P) = 84{,}0\,(15)°$ verbundene Stauchung des Oktaeders WP_6 in Richtung der dreizähligen Achse beobachtet. Diese führt zu einer ringförmigen Anordnung der Phosphor- und Fluoratome um das Wolframatom. Die Fluoratome benachbarter PF_2Ph-Gruppen nähern sich dabei bis auf einen Abstand von 2,812 Å. Zusammen mit den Phenylringen oberhalb und unterhalb der PF-Ringebene ergibt sich eine vollständige Abschirmung des Zentralatoms.



(I)

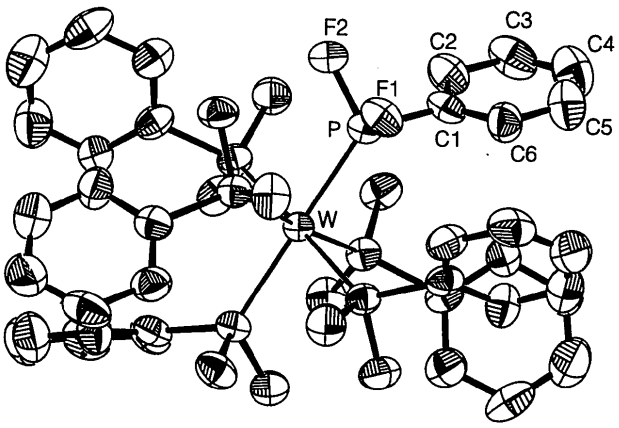


Fig. 1. $W(PF_2Ph)_6$. Komplex mit der Atombenennung und den thermischen Ellipsoiden (diese umschreiben den Ort mit 50% Aufenthaltswahrscheinlichkeit für den Mittelpunkt des Atoms bei $T = 298$ K).

Ein bemerkenswerter Aspekt in der Struktur des $W(PF_2Ph)_6$ ist der relativ kurze Bindungsabstand $d(W—P) = 2{,}375\,(2)$ Å. Die Bindungsverkürzung wird im Vergleich mit den Daten der bisher bekannten homogenen Phosphankomplexe $W(PMe_3)_6$ mit $d(W—P) = 2{,}455\,(5)$ Å (Rabinovich & Parkin, 1990), $W(dmpe)_3$ mit $d(W—P) = 2{,}414\,(6)$ Å (Cloke, Fyne, Gibson, Green, Ledoux, Perutz, Dix, Gourdon & Prout, 1984) und $W(PF_2{}^tBu)_6$ mit $d(W—P) = 2{,}417(6)$ Å (Krampe *et al.*, 1989) deutlich. Dem Liganden PF_2Ph kann folglich in dieser Reihe die höchste π-Akzeptortendenz zugesprochen werden. Die Bindungsgeometrie um die Phosphoratome folgt dem bereits im $W(PF_2{}^tBu)_6$ beobachteten Trend mit einer deutlichen Verzerrung der Tetraedergeometrie [$\varphi(F—P—F) = 95{,}6\,(3)$, $\varphi(W—P—F) = 116{,}1\,(3)$, $115{,}7\,(2)$ und $\varphi(W—P—C) = 126{,}8\,(3)°$]. Die übrigen geometrischen Parameter der Phosphanliganden entsprechen der Erwartung.

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