Lists of structure factors, anisotropic displacement parameters, least-squares-planes data and complete geometry have been deposited with the IUCr (Reference: BK1033). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Trichlorotin(II)-(*meso*-Tetraphenyl-porphyrinato)rhodium(III), a Porphyrin Derivative with an Rh—Sn Bond

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## Abstract

The structure of the title compound, trichloro-$2\kappa^3 Cl$-(5,10,15,20-tetraphenylporphyrinato-$1\kappa^4 N^{21,22,23,24}$)rhodium(III)tin(II)(*Rh—Sn*), [RhSnCl₃(C₄₄H₂₈N₄)], consists of well separated units in which the Rh atom is five-coordinate at the center of a square-pyramidal polyhedron with the Sn atom at the top. The macrocylic

unit is planar with the Rh atom displaced by only 0.02 Å from the ring plane. The Rh—Sn bond length is 2.450 (1) Å.

Comment

Metal–porphyrin derivatives containing metal–metal bonds have attracted interest because of their biological implications and their possible applications as unidirectional electron-conducting materials (Onaka *et al.*, 1985). We have reported the synthesis and spectroscopic characterization of [(TPP)RhX] derivatives, where X represents axial ligands containing different metal groups and TPP is tetraphenylporphyrinato (Boschi, Licoccia, Paolesse & Tagliatesta, 1988); while detailed structures of such complexes are not known, the true nature of the metal–metal bond may be a matter of debate. We report here the single-crystal X-ray characterization of the complex [(TPP)RhSnCl₃] (I).

(I)
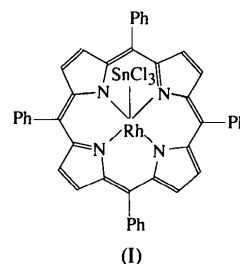
Rh resides at the center of the TPP macrocylic ligand; the environment of Rh is five-coordinate and is described as square-pyramidal with the —SnCl₃ ligand at the apex. The Rh atom is displaced by only 0.02 Å from the mean plane of the 16-atom core of the porphyrin, towards Sn; the largest deviations from this plane are −0.16 Å for C(16) and 0.18 Å for C(1). The Rh—Sn bond length [2.450 (1) Å] is outside the wide range (2.53–2.72 Å) of previously determined Rh—Sn distances (Hawkins, Hitchcock & Lappert, 1985; Balch, Hope & Wood, 1985; Chan & Marder, 1988; Veith, Stahl & Huch, 1989; Bott, Machell, Mingos & Watson, 1991) and this shorter distance could reflect a greater degree of Rh—Sn π bonding. The coordination geometry about the Sn atom is distorted from ideal tetrahedral, the Rh—Sn—Cl angles being 116.9 (1), 116.0 (2) and 114.8 (1)° and the Cl—Sn—Cl angles averaging 102.3 (1)°. The same feature is seen for other —SnCl₃ ligands coordinated to transition metals (Holt, Wilson & Nelson, 1989). The Rh—N mean distance of 2.02 Å is similar to those reported for other rhodium porphyrinates, such as [(EPI)Rh(Me₂NH)₂]⁺ (Hanson, Gouterman & Hanson, 1973), [(OEP)RhMe] (Takenaka *et al.*, 1976) and [(EPI)Rh(PHCO)] (Grigg, Trocha-Grimshaw & Henrick, 1982); furthermore, the bond lengths and angles in the porphyrinato core are in good agreement with those reported for several other metallo-

porphyrin structures. The crystal is built up by the juxtaposition at van der Waals distances of well separated units, as shown in Fig. 1(b), and no unusual nonbonded interactions are evident.
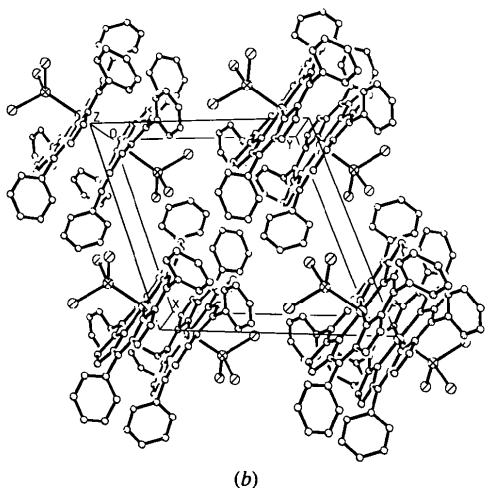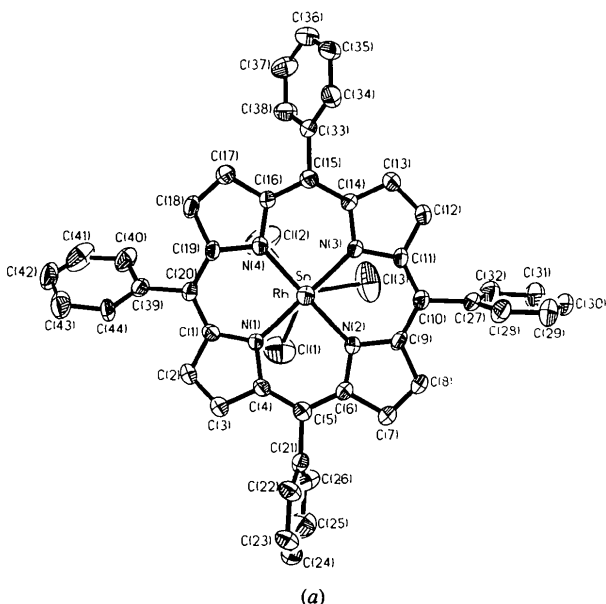

(a)

(b)

Fig. 1. (a) *ORTEP* (Johnson, 1965) diagram of [(TPP)RhSnCl₃], with atom-numbering scheme and displacement ellipsoids at the 40% probability level; (b) molecular packing in the unit cell.

Experimental

Anhydrous $SnCl_2$ and (TPP)RhCl (molar ratio 1.2:1) were dissolved in THF and the solution stirred overnight. Suitable crystals for analysis were obtained by slow diffusion of *n*-hexane into a diethyl ether solution of the complex.

Crystal data

[RhSnCl₃(C₄₄H₂₈N₄)]
$M_r = 940.7$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Triclinic
$P\bar{1}$
$a = 12.719\,(2)$ Å
$b = 12.906\,(2)$ Å
$c = 16.930\,(3)$ Å
$\alpha = 68.20\,(2)°$
$\beta = 68.23\,(2)°$
$\gamma = 64.08\,(2)°$
$V = 2247.5\,(7)$ Å^3
$Z = 2$
$D_x = 1.390$ Mg m^{-3}

Cell parameters from 50 reflections
$\theta = 8–13°$
$\mu = 1.13$ mm^{-1}
$T = 294$ K
Parallelepiped
$0.30 \times 0.20 \times 0.15$ mm
Violet

Data collection

Siemens *R3m/V* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (ψ scans)
$T_{min} = 0.86$, $T_{max} = 1.00$
8311 measured reflections
7926 independent reflections
4754 observed reflections $[F > 4\sigma(F)]$

$R_{int} = 0.027$
$\theta_{max} = 25°$
$h = 0 \rightarrow 15$
$k = -13 \rightarrow 15$
$l = -18 \rightarrow 20$
2 standard reflections monitored every 150 reflections
intensity decay: none

Refinement

Refinement on F
$R = 0.057$
$wR = 0.080$
$S = 1.72$
4754 reflections
479 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.0016F^2]$

$(\Delta/\sigma)_{max} = 0.02$
$\Delta\rho_{max} = 1.37$ e Å^{-3}
$\Delta\rho_{min} = -1.08$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	y	z	U_{eq}
Sn	0.2054 (1)	0.1974 (1)	0.2390 (1)	0.041 (1)
Cl(1)	0.1036 (4)	0.3935 (3)	0.1775 (3)	0.110 (2)
Cl(2)	0.3199 (4)	0.2204 (5)	0.3064 (3)	0.130 (3)
Cl(3)	0.3440 (4)	0.1330 (4)	0.1181 (3)	0.127 (3)
Rh	0.0825 (1)	0.0739 (1)	0.3355 (1)	0.049 (1)
N(1)	−0.0611 (6)	0.2204 (6)	0.3619 (4)	0.038 (3)
N(2)	0.0260 (6)	0.0855 (6)	0.2345 (4)	0.040 (3)
N(3)	0.2253 (6)	−0.0719 (6)	0.3097 (4)	0.040 (3)
N(4)	0.1287 (6)	0.0504 (6)	0.4433 (5)	0.041 (3)
C(1)	−0.0801 (7)	0.2770 (8)	0.4232 (6)	0.041 (4)
C(2)	−0.1763 (8)	0.3922 (8)	0.4077 (6)	0.050 (5)
C(3)	−0.2148 (8)	0.3973 (9)	0.3423 (7)	0.052 (5)
C(4)	−0.1432 (7)	0.2921 (7)	0.3114 (6)	0.041 (4)
C(5)	−0.1542 (7)	0.2661 (8)	0.2428 (6)	0.044 (4)
C(6)	−0.0765 (8)	0.1691 (8)	0.2088 (6)	0.045 (4)
C(7)	−0.0869 (9)	0.1424 (9)	0.1365 (6)	0.055 (5)
C(8)	0.0079 (9)	0.0477 (9)	0.1199 (6)	0.053 (5)
C(9)	0.0809 (8)	0.0097 (8)	0.1792 (6)	0.045 (5)
C(10)	0.1901 (7)	−0.0819 (8)	0.1796 (6)	0.044 (4)
C(11)	0.2591 (7)	−0.1173 (8)	0.2380 (5)	0.040 (4)
C(12)	0.3779 (8)	−0.2086 (9)	0.2358 (6)	0.052 (5)
C(13)	0.4143 (8)	−0.2160 (9)	0.3043 (7)	0.053 (5)
C(14)	0.3188 (7)	−0.1338 (8)	0.3520 (5)	0.041 (4)
C(15)	0.3180 (8)	−0.1200 (7)	0.4296 (6)	0.042 (4)
C(16)	0.2248 (7)	−0.0378 (7)	0.4746 (5)	0.038 (4)
C(17)	0.2212 (8)	−0.0295 (8)	0.5579 (6)	0.049 (5)
C(18)	0.1224 (8)	0.0677 (8)	0.5766 (6)	0.047 (5)

C(19)	0.0694 (7)	0.1228 (7)	0.5031 (5)	0.038 (4)
C(20)	−0.0242 (7)	0.2321 (7)	0.4908 (5)	0.038 (4)
C(21)	−0.2574 (9)	0.3531 (8)	0.2020 (7)	0.052 (5)
C(22)	−0.3710 (8)	0.3435 (11)	0.2443 (7)	0.067 (6)
C(23)	−0.4701 (10)	0.4270 (16)	0.2071 (11)	0.095 (9)
C(24)	−0.4553 (13)	0.5128 (12)	0.1377 (11)	0.082 (8)
C(25)	−0.3422 (17)	0.5191 (12)	0.0968 (11)	0.105 (11)
C(26)	−0.2446 (12)	0.4407 (11)	0.1300 (9)	0.079 (8)
C(27)	0.2368 (8)	−0.1524 (8)	0.1116 (6)	0.046 (4)
C(28)	0.1850 (10)	−0.2335 (9)	0.1222 (7)	0.059 (6)
C(29)	0.2304 (11)	−0.2973 (11)	0.0588 (9)	0.076 (7)
C(30)	0.3223 (11)	−0.2802 (13)	−0.0114 (9)	0.082 (8)
C(31)	0.3759 (12)	−0.2001 (13)	−0.0226 (8)	0.085 (8)
C(32)	0.3316 (10)	−0.1374 (12)	0.0414 (8)	0.075 (7)
C(33)	0.4256 (8)	−0.1942 (8)	0.4672 (6)	0.044 (4)
C(34)	0.4595 (8)	−0.3177 (9)	0.4989 (7)	0.054 (5)
C(35)	0.5581 (9)	−0.3795 (9)	0.5317 (6)	0.056 (5)
C(36)	0.6258 (9)	−0.3265 (10)	0.5343 (7)	0.065 (6)
C(37)	0.5923 (10)	−0.2044 (11)	0.5058 (8)	0.071 (7)
C(38)	0.4942 (9)	−0.1400 (9)	0.4720 (7)	0.061 (6)
C(39)	−0.0576 (8)	0.3055 (8)	0.5530 (6)	0.044 (4)
C(40)	0.0301 (11)	0.3373 (10)	0.5592 (7)	0.064 (6)
C(41)	−0.0056 (17)	0.4076 (11)	0.6181 (10)	0.089 (10)
C(42)	−0.1104 (15)	0.4368 (11)	0.6693 (9)	0.079 (8)
C(43)	−0.2003 (15)	0.4048 (11)	0.6654 (8)	0.091 (8)
C(44)	−0.1708 (9)	0.3393 (8)	0.6052 (6)	0.054 (5)

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

Sn—Rh	2.450 (1)	Sn—Cl(1)	2.313 (3)
Sn—Cl(2)	2.318 (7)	Sn—Cl(3)	2.301 (4)
Rh—N(1)	2.028 (6)	Rh—N(2)	2.022 (9)
Rh—N(3)	2.017 (6)	Rh—N(4)	2.000 (9)
Cl(1)—Sn—Rh	116.9 (1)	Cl(2)—Sn—Rh	114.8 (1)
Cl(3)—Sn—Rh	116.0 (2)	Sn—Rh—N(1)	90.8 (2)
Sn—Rh—N(2)	91.7 (2)	Sn—Rh—N(3)	89.3 (2)
Sn—Rh—N(4)	94.4 (2)	N(1)—Rh—N(2)	90.3 (3)
N(2)—Rh—N(3)	89.9 (3)	N(3)—Rh—N(4)	89.6 (3)
N(1)—Rh—N(4)	90.2 (3)	N(1)—Rh—N(3)	179.7 (4)
N(2)—Rh—N(4)	173.8 (3)		

Structure solution and refinement: *SHELXTL-Plus* (Sheldrick, 1991).

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Bis(3-methylpyridine)bis[4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionato]nickel(II)

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Abstract

In the title compound, [Ni(C$_8$H$_4$F$_3$O$_2$S)$_2$(C$_6$H$_7$N)$_2$], the Ni atom displays distorted octahedral coordination to four coplanar O atoms from two trifluorothienylbutanedione ligands and two apical 3-methylpyridine N atoms. The two trifluorothienylbutanedione ligands, and hence the two thiophene rings, are *cis* oriented with respect to each other, whereas the 3-methylpyridine ligands are mutually *trans*. The Ni—N(1) and Ni—N(2) bond distances are 2.090 (6) and 2.104 (6) Å, respectively, and the four Ni—O distances are in the range 2.024 (5) to 2.045 (5) Å.

Comment

4,4,4-Trifluoro-1-(2-thienyl)-1,3-butanedione (TTA) has been used as a lubrication additive for Cu–Cu and Cu–Fe friction couples in bearings (Kuzharov, Suchkov & Komarchuk, 1983), and its metal complex, [Cu(TTA)$_2$], was also found to be a selective metal-transfer lubrication additive (Kuzharov, Suchkov, Kozakov & Nikol'skii, 1989). [*M*(TTA)$_2$] complexes, well known