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Acta Cryst. (1994). C**50**, 889–891

(Pyridine-2-thiolato-*N*,*S*)bis(triphenylphosphine)platinum(II) Hexafluorophosphate Chloroform Solvate

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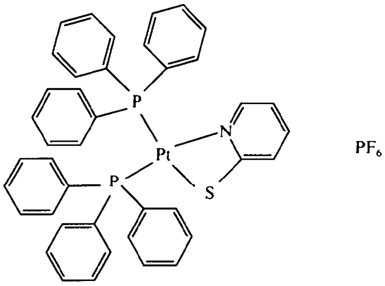
(*Received* 21 *June* 1993; *accepted* 25 *October* 1993)

Abstract

The first structure determination of a monomeric platinum complex with a pyridine-2-thiolato ligand is reported. The Pt atom in (pyridine-2-thiolato-*N*,*S*)bis(triphenylphosphine)platinum(II) hexafluorophosphate chloroform solvate, $[Pt(C_5H_4NS)(PPh_3)_2]PF_6.CHCl_3$, is coordinated by two triphenylphosphine ligands and a pyridine-2-thiolato ligand through N and S atoms.

Comment

It has been demonstrated that the deprotonated 2-mercaptopyridine ligand C_5H_4NS functions either as a monodentate ligand, a bidentate chelating ligand or a bridging ligand when coordinated to metal centers (Deeming, Karim, Bates & Hursthouse, 1988). Recently, we have synthesized two mercury(II) complexes containing the pyridine-2-thiolato ligand, $Hg(C_5H_4NS)(O_2CCH_3)$ and $Hg(C_5H_4NS)_2$ (Wang & Fackler, 1989). Both compounds have one-dimensional structures in the solid phase. $Hg(C_5H_4NS)_2$ is especially interesting as the N atom on the C_5H_4NS ligand does not coordinate to the Hg center, thus enabling it to bind to a second metal center to form bimetallic compounds. We carried out the reaction of $Hg(C_5H_4NS)_2$ with $Pt(PPh_3)_2Cl_2$ in the presence of $TlPF_6$ hoping to obtain an HgPt bimetallic complex. Bimetallic platinum complexes have been reported in which the pyridine-2-thiolate ligand acts as a bridge between the metal centers (Umakoshi, Kinoshita, Fukui-Yasuba, Matsumoto, Ooi, Nakai & Shiro, 1989). The yellow product obtained from this reaction was analyzed by single-crystal X-ray diffraction, which showed the product to be $[Pt(C_5H_4NS)(PPh_3)_2]PF_6$, (1). Although this was not the bimetallic compound we expected, the synthesis and the structure of a monomeric platinum(II) complex containing pyridine-2-thiolate have not been reported previously.



(I)

The molecular structure of $[Pt(C_5H_4NS)(PPh_3)_2]PF_6$ is shown in Fig. 1. The Pt atom is coordinated by two triphenylphosphine ligands and one C_5H_4NS ligand through the N and S atoms with a distorted square-planar geometry [P(1)—Pt—S = 165.6 (1), P(2)—Pt—N = 163.8 (2)°]. Although the Pt—P distances are normal, the Pt—P(1) distance [2.295 (2) Å] is slightly longer than the Pt—P(2) distance [2.253 (2) Å], apparently as a result of the stronger *trans* effect of the S atom relative to N. The S—C(5) distance of 1.735 (7) Å is typical for an

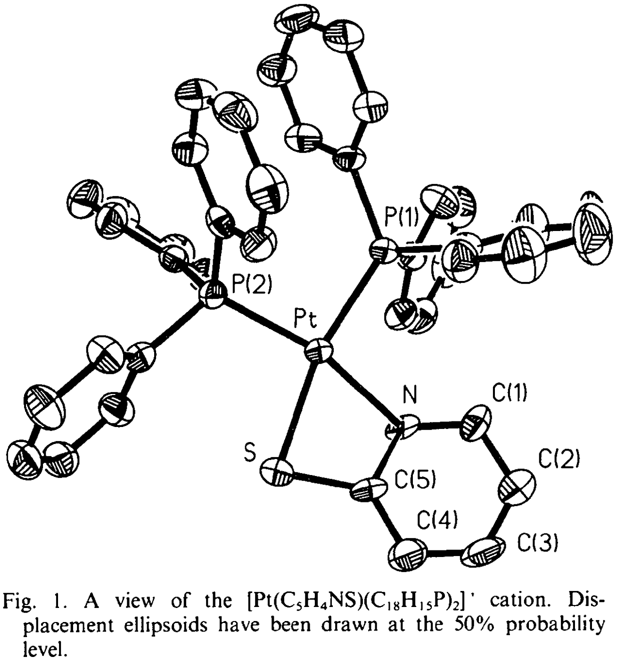


Fig. 1. A view of the $[Pt(C_5H_4NS)(C_{18}H_{15}P)_2]^+$ cation. Displacement ellipsoids have been drawn at the 50% probability level.

Acta Crystallographica Section C
ISSN 0108-2701 ©1994

S—C single bond. The bite angle of S—C(5)—N [108.8 (5)°] is much smaller than that in $Hg(C_5H_4NS)(O_2CCH_3)$ [119 (1)°] or those in the platinum(II) dimers (120.6 to 124.0°), where C_5H_4NS is a bridging ligand, or that in $Hg(C_5H_4NS)_2$ [117.6 (7)°], where C_5H_4NS is a monodentate ligand through the S atom. The smaller S—C—N angle is apparently caused by the chelating effect of the ligand. The bond lengths and angles of the PF_6^- anion are normal. Neither the PF_6^- anion nor the $CHCl_3$ molecule show any significant disorder.

Experimental

$[Pt(C_5H_4NS)(PPh_3)_2]PF_6$ was prepared by the reaction of $Hg(C_5H_4NS)_2$ with two equivalents of $Pt(PPh_3)_2Cl_2$ in the presence of $TlPF_6$ in CH_2Cl_2. $Pt(PPh_3)_2Cl_2$ (19 mg, 0.024 mmol) was added to a solution of $Hg(C_5H_4NS)_2$ (5 mg, 0.012 mmol) in CH_2Cl_2. The mixture was stirred for 5 h at 295 K. After filtration, a light yellow solution was obtained. Excess diethyl ether and hexane were added to this solution. Crystallization at 273 K produced yellow crystals of (1). Single crystals suitable for X-ray diffraction analysis were grown from $CHCl_3$/diethyl ether at 273 K.

Crystal data

$[Pt(C_5H_4NS)(C_{18}H_{15}P)_2]$-$PF_6.CHCl_3$
$M_r = 1094.2$
Triclinic
$P\bar{1}$
$a = 10.613$ (1) Å
$b = 13.313$ (3) Å
$c = 15.272$ (3) Å
$\alpha = 92.96$ (2)°
$\beta = 94.73$ (1)°
$\gamma = 92.75$ (2)°
$V = 2144.7$ (6) Å^3

$Z = 2$
$D_x = 1.69$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 15$-20°
$\mu = 3.85$ mm^{-1}
$T = 293$ K
Rectangular
0.3 × 0.2 × 0.2 mm
Yellow

Data collection

Nicolet *R3m/E* diffractometer
Wyckoff scans
Absorption correction: empirical
$T_{\min} = 0.419$, $T_{\max} = 1.000$
5617 measured reflections
5276 independent reflections
4698 observed reflections $[F_o^2 > 3\sigma(F_o^2)]$

$R_{\rm int} = 0.0524$
$\theta_{\max} = 22.5$°
$h = -12 \rightarrow 12$
$k = -15 \rightarrow 0$
$l = -17 \rightarrow 17$
2 standard reflections monitored every 198 reflections intensity variation: 3%

Refinement

Refinement on F
$R = 0.0399$
$wR = 0.0521$
$S = 1.241$
4698 reflections
514 parameters

$\Delta\rho_{\max} = 1.51$ e Å^{-3}
$\Delta\rho_{\min} = -1.04$ e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficients: primary = 0.0, secondary = 0.0

H-atom parameters not refined
$w = 1/[\sigma^2(F_o) + 0.00140F_o^2]$
$(\Delta/\sigma)_{\max} = 0.006$

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)

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

	x	y	z	$U_{\rm eq}$
Pt	0.0818 (1)	0.2284 (1)	0.1830 (1)	0.028 (1)
P(1)	0.0560 (2)	0.1342 (1)	0.3025 (1)	0.032 (1)
P(2)	0.2717 (2)	0.1737 (1)	0.1520 (1)	0.030 (1)
P(3)	0.5440 (2)	0.6491 (2)	0.3519 (2)	0.058 (1)
S	0.0566 (2)	0.3364 (2)	0.0667 (1)	0.041 (1)
Cl(1)	0.1430 (3)	0.5119 (2)	0.2785 (2)	0.080 (1)
Cl(2)	0.0557 (4)	0.6988 (3)	0.2172 (3)	0.133 (2)
Cl(3)	0.2260 (5)	0.5860 (4)	0.1191 (3)	0.165 (2)
F(1)	0.4888 (6)	0.7255 (5)	0.2819 (4)	0.093 (3)
F(2)	0.5946 (7)	0.5742 (5)	0.4196 (5)	0.117 (3)
F(3)	0.5909 (6)	0.7434 (5)	0.4171 (4)	0.093 (3)
F(4)	0.4967 (6)	0.5564 (4)	0.2852 (4)	0.091 (2)
F(5)	0.4105 (6)	0.6480 (6)	0.3919 (4)	0.107 (3)
F(6)	0.6743 (5)	0.6561 (5)	0.3081 (4)	0.092 (3)
N	−0.0798 (5)	0.3134 (4)	0.1908 (4)	0.029 (2)
C	0.1886 (12)	0.6164 (9)	0.2218 (7)	0.088 (5)
C(1)	−0.1678 (7)	0.3270 (7)	0.2515 (5)	0.051 (3)
C(2)	−0.2476 (8)	0.4078 (7)	0.2432 (6)	0.058 (3)
C(3)	−0.2342 (8)	0.4716 (7)	0.1755 (6)	0.060 (3)
C(4)	−0.1451 (7)	0.4552 (6)	0.1147 (5)	0.050 (3)
C(5)	−0.0680 (6)	0.3738 (5)	0.1253 (5)	0.037 (2)
C(10)	−0.0831 (6)	0.0475 (5)	0.2808 (5)	0.037 (2)
C(11)	−0.1084 (8)	−0.0274 (6)	0.3372 (5)	0.053 (3)
C(12)	−0.2145 (8)	−0.0934 (7)	0.3217 (6)	0.060 (3)
C(13)	−0.2953 (8)	−0.0830 (7)	0.2469 (6)	0.058 (3)
C(14)	−0.2683 (7)	−0.0118 (7)	0.1896 (6)	0.055 (3)
C(15)	−0.1625 (6)	0.0545 (6)	0.2058 (5)	0.042 (3)
C(20)	0.0288 (6)	0.2179 (6)	0.3962 (5)	0.039 (2)
C(21)	−0.0621 (8)	0.1958 (7)	0.4545 (6)	0.063 (3)
C(22)	−0.0714 (11)	0.2640 (9)	0.5254 (7)	0.091 (5)
C(23)	0.0117 (12)	0.3476 (9)	0.5408 (7)	0.089 (5)
C(24)	0.0973 (10)	0.3693 (7)	0.4830 (6)	0.071 (4)
C(25)	0.1069 (8)	0.3052 (6)	0.4108 (5)	0.051 (3)
C(30)	0.1761 (6)	0.0531 (5)	0.3473 (4)	0.035 (2)
C(31)	0.2489 (7)	0.0790 (6)	0.4266 (5)	0.042 (3)
C(32)	0.3353 (7)	0.0133 (7)	0.4589 (5)	0.054 (3)
C(33)	0.3536 (8)	−0.0756 (7)	0.4144 (6)	0.061 (3)
C(34)	0.2837 (8)	−0.1027 (6)	0.3363 (6)	0.052 (3)
C(35)	0.1939 (7)	−0.0389 (6)	0.3027 (5)	0.045 (3)
C(40)	0.3421 (6)	0.2435 (5)	0.0668 (4)	0.035 (2)
C(41)	0.2835 (7)	0.2309 (6)	−0.0190 (4)	0.042 (3)
C(42)	0.3343 (8)	0.2818 (6)	−0.0864 (5)	0.049 (3)
C(43)	0.4405 (8)	0.3438 (6)	−0.0692 (6)	0.054 (3)
C(44)	0.4993 (8)	0.3554 (7)	0.0133 (6)	0.056 (3)
C(45)	0.4500 (7)	0.3067 (6)	0.0830 (5)	0.045 (3)
C(50)	0.2680 (6)	0.0442 (5)	0.1062 (4)	0.031 (2)
C(51)	0.1508 (7)	−0.0063 (5)	0.0836 (5)	0.041 (3)
C(52)	0.1460 (8)	−0.1041 (6)	0.0445 (5)	0.053 (3)
C(53)	0.2565 (9)	−0.1491 (7)	0.0289 (5)	0.063 (3)
C(54)	0.3724 (8)	−0.0970 (7)	0.0488 (6)	0.056 (3)
C(55)	0.3774 (7)	−0.0019 (6)	0.0865 (5)	0.045 (3)
C(60)	0.3874 (6)	0.1935 (5)	0.2474 (4)	0.030 (2)
C(61)	0.3911 (6)	0.2895 (6)	0.2907 (5)	0.041 (3)
C(62)	0.4775 (8)	0.3138 (7)	0.3624 (5)	0.052 (3)
C(63)	0.5607 (7)	0.2436 (7)	0.3900 (5)	0.053 (3)
C(64)	0.5589 (7)	0.1507 (7)	0.3472 (5)	0.053 (3)
C(65)	0.4720 (7)	0.1240 (6)	0.2757 (5)	0.042 (3)

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

Pt—P(1)	2.295 (2)	Pt—P(2)	2.253 (2)
Pt—S	2.348 (2)	Pt—N	2.108 (5)
P(1)—C(10)	1.828 (7)	P(1)—C(20)	1.818 (7)

P(1)—C(30)	1.823 (7)	P(2)—C(40)	1.826 (7)
P(2)—C(50)	1.825 (7)	P(2)—C(60)	1.825 (6)
P(3)—F(1)	1.608 (7)	P(3)—F(2)	1.556 (8)
P(3)—F(3)	1.596 (6)	P(3)—F(4)	1.592 (6)
P(3)—F(5)	1.589 (7)	P(3)—F(6)	1.585 (7)
S—C(5)	1.735 (7)	Cl(1)—C	1.746 (12)
Cl(2)—C	1.828 (13)	Cl(3)—C	1.683 (12)
N—C(1)	1.381 (10)	N—C(5)	1.325 (9)
C(1)—C(2)	1.405 (12)	C(2)—C(3)	1.382 (13)
C(3)—C(4)	1.396 (12)	C(4)—C(5)	1.397 (11)
P(1)—Pt—P(2)	97.4 (1)	P(1)—Pt—S	165.6 (1)
P(2)—Pt—S	97.0 (1)	P(1)—Pt—N	97.8 (2)
P(2)—Pt—N	163.8 (2)	S—Pt—N	68.0 (2)
Pt—P(1)—C(10)	110.1 (2)	Pt—P(1)—C(20)	109.0 (3)
C(10)—P(1)—C(20)	107.5 (3)	Pt—P(1)—C(30)	123.1 (2)
C(10)—P(1)—C(30)	102.6 (3)	C(20)—P(1)—C(30)	103.4 (3)
Pt—P(2)—C(40)	112.9 (2)	Pt—P(2)—C(50)	114.7 (2)
C(40)—P(2)—C(50)	102.1 (3)	Pt—P(2)—C(60)	111.1 (2)
C(40)—P(2)—C(60)	104.1 (3)	C(50)—P(2)—C(60)	111.2 (3)
F(1)—P(3)—F(2)	178.8 (4)	F(1)—P(3)—F(3)	89.1 (3)
F(2)—P(3)—F(3)	91.5 (4)	F(1)—P(3)—F(4)	89.8 (3)
F(2)—P(3)—F(4)	89.6 (4)	F(3)—P(3)—F(4)	178.9 (4)
F(1)—P(3)—F(5)	87.7 (4)	F(2)—P(3)—F(5)	91.3 (4)
F(3)—P(3)—F(5)	89.4 (4)	F(4)—P(3)—F(5)	90.8 (4)
F(1)—P(3)—F(6)	88.6 (4)	F(2)—P(3)—F(6)	92.5 (4)
F(3)—P(3)—F(6)	89.9 (3)	F(4)—P(3)—F(6)	89.8 (4)
F(5)—P(3)—F(6)	176.2 (4)	Pt—S—C(5)	81.3 (2)
Pt—N—C(1)	135.3 (5)	Pt—N—C(5)	101.3 (4)
C(1)—N—C(5)	122.4 (6)	Cl(1)—C—Cl(2)	106.9 (7)
Cl(1)—C—Cl(3)	113.2 (7)	Cl(2)—C—Cl(3)	109.7 (6)
N—C(1)—C(2)	118.6 (8)	C(1)—C(2)—C(3)	119.1 (8)
C(2)—C(3)—C(4)	121.0 (8)	C(3)—C(4)—C(5)	118.0 (8)
S—C(5)—N	108.8 (5)	S—C(5)—C(4)	130.1 (6)
N—C(5)—C(4)	121.0 (7)		

The crystal used for the study was mounted on a glass fiber with epoxy. The diffractometer was controlled by a Data General Nova 4 minicomputer. Triclinic symmetry was suggested from interaxial angles and by Delaunay reduction. Axial lengths were confirmed by comparison with interlayer spacings observed in axial photographs. Backgrounds were estimated from a 96-step peak profile. The data were corrected for decay by scaling on the standard reflections (both decayed similarly). Data were also corrected for Lorentz and polarization effects. Absorption corrections were based on seven reflections spanning a range of 2θ values from 10.75 to 32.63°. Crystal structure solution and refinement were carried out using the *SHELXTL* collection of crystallographic software (Sheldrick, 1985) on a Data General Eclipse S140 minicomputer. The coordinates of the Pt atom were determined from a Patterson map. All remaining non-H atoms were obtained from subsequent difference Fourier maps. The positions of H atoms on the phenyl rings were calculated by using a fixed C—H distance of 0.96 Å. A chloroform solvent molecule was located and refined successfully. All non-H atoms were refined anisotropically.

These studies were supported by the Welch Foundation and the National Science Foundation (grant CHE 8708625).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71779 (38 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1051]

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Acta Cryst. (1994). **C50**, 891–893

Tris(*tert*-butylcyclopentadienyl)neodymium-μ-chloro-tris(tetrahydrofuran)lithium, [Nd(η^5-^{t}BuCp)$_3$(μ-Cl)Li(thf)$_3$]

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(*Received* 6 *June* 1993; *accepted* 26 *October* 1993)

Abstract

The title complex, tris[2(η^5)-*tert*-butylcyclopentadienyl]-μ-chloro-1:2κ^2*Cl*-tris(tetrahydrofuran-1κ*O*)lithiumneodymium, $[\mathrm{Nd(C_9H_{13})_3(\mu\text{-}Cl)Li(C_4H_8O)_3}]$, consists of the neutral moiety (^{t}BuCp)$_3$Nd linked to the cation $[\mathrm{Li(thf)_3}]^+$ by a μ-Cl bridge. The Nd atom is coordinated by three η^5-bonded *tert*-butylcyclopentadienyl (^{t}BuCp) ligands and a $\mathrm{Cl^-}$ ion to form a slightly deformed tetrahedron. Nd—Cl = 2.797 (2), Li—Cl = 2.345 (9) Å and Nd—Cl—Li = 141.4 (3)°.

Comment

The synthesis and structures of Cp$_3$Ln and Cp$_3$Ln*L* complexes (Cp = cyclopentadienyl, Ln = lanthanide, *L* = neutral ligand) have been reported for all the rare-earth elements (Birmingham & Wilkinson, 1956; Eggers, Kopf & Fischer, 1986). $[\mathrm{Cp_3PrC_4H_9}]^-$ (Jahn, Yünlü, Oroschin, Amberger & Fischer, 1984), $[\mathrm{Cp_3NdC_6H_5}]^-$ (Gao, Shen, Hu, Jin & Lin, 1992) and $[\mathrm{Cp_3LnCH_3}]^-$ (Ln = La, Nd) (Guan, Hu & Shen, 1991) have also been reported. Recently, we described the complex [(η^5-^{t}BuCp)$_3$Nd(μ-Br)Li(thf)$_3$] (thf = tetrahydrofuran) (Song, Shen & Jin, 1992) and now report the structure of the analogous species