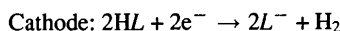


Table 2. Geometric parameters (Å, °)

Mn1—Cl1	2.235 (1)	O2—C101	1.321 (4)
Mn1—O1	1.866 (3)	N1—C7	1.298 (4)
Mn1—O2	1.858 (3)	N1—C8	1.444 (5)
Mn1—N1	2.143 (3)	N2—C107	1.289 (4)
Mn1—N2	2.158 (3)	N2—C108	1.436 (5)
O1—C1	1.323 (4)		
Cl1—Mn1—O1	118.81 (8)	O1—Mn1—N1	86.8 (1)
Cl1—Mn1—O2	119.74 (8)	O1—Mn1—N2	92.3 (1)
Cl1—Mn1—N1	98.13 (7)	O2—Mn1—N1	85.0 (1)
Cl1—Mn1—N2	91.57 (8)	O2—Mn1—N2	86.5 (1)
O1—Mn1—O2	121.44 (9)	N1—Mn1—N2	169.41 (9)

The Schiff base, *N*-salicyldenephylamine (HL), was prepared by refluxing equimolar amounts of salicylaldehyde and aniline in chloroform until the expected amount of water was collected in a Dean–Stark trap. After checking its purity using IR and ¹H NMR spectra, the Schiff base was used to prepare [MnL₂phen] by an electrochemical method similar to that described by Habeeb, Tuck & Walters (1978). The electrochemical oxidation of manganese was carried out in a 100 ml 'tall-form' beaker with a solution of 0.27 g of HL (1.37 mmol), 0.121 g of 1,10-phenanthroline (phen) (6.72 mmol) and 10 mg of tetraethylammonium perchlorate in 50 ml of acetonitrile by applying a voltage of 10 V and a current of 20 mA for 1.83 h. The cell can be summarized as Pt⁻/CH₃CN + HL/Mn⁺. The reaction mixture was subsequently filtered to remove metal particles and the filtrate concentrated by low-pressure evaporation at room temperature. The solid, [MnL₂phen], thus formed was washed with acetonitrile and dried. Analysis: found C, 72.7; H, 4.4; N, 8.9. Calculated for [Mn(C₁₃H₁₀NO)₂(C₁₂H₈N₂)]: C, 72.7; H, 4.5; N, 8.9. The electrochemical efficiency of 0.56 mol Faraday⁻¹ derived from the volume of hydrogen evolved at the cathode is compatible with the following reaction scheme:



Tetrachloroferrate-ferrocenium was prepared by the addition of a solution of ferrocene (0.2 mol) in 600 ml anhydrous ethyl ether to a suspension of anhydrous FeCl₃ (0.4 mol) in 300 ml of the same solvent. After stirring, a blue-green precipitate formed; this was filtrated and dried *in vacuo*. [MnL₂Cl] was obtained by the chemical oxidation of [MnL₂phen] with Cp₂Fe⁺.FeCl₄⁻. A solution of Cp₂Fe⁺.FeCl₄⁻ (0.176 g, 0.459 mmol) in acetonitrile was added to a suspension of [MnL₂phen] (0.288, 0.459 mmol) in the same solvent. The reaction mixture was stirred until a clear solution was obtained, which was reduced in volume by 75% followed by the addition of diethyl ether to precipitate a solid. The solid was filtered and the remaining solution concentrated by slow evaporation at room temperature to give X-ray quality crystals of [MnL₂Cl]. Analysis: found C, 65.3; H, 4.0; N, 5.9; Calculated for [Mn(C₁₃H₁₀NO)₂Cl]: C, 64.7; H, 4.1; N, 5.8.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55764 (36 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1035]

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cis-Dichloro(di-*n*-butyl sulfide)(tri-*n*-butylphosphine)platinum(II)

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Abstract

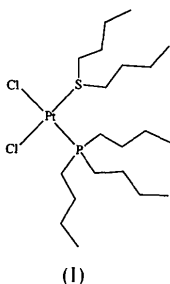
cis-Dichloro(di-*n*-butyl sulfide)(tri-*n*-butylphosphine)-platinum(II) was prepared by reacting *sym-trans*-[Pt₂Cl₄(PBU₃)₂] with two equivalents of di-*n*-butyl sulfide in dichloromethane solution. The complex has a square-planar structure with the two neutral ligands in *cis* positions.

Comment

We are interested in simple platinum compounds containing phosphine and sulfide ligands as models

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for adducts formed between the enzyme soybean lipoxygenase-1 and its inhibitor, the Pt^{II} complex NEt₄[PtCl₃(PBU₃⁺)] (Michaud-Soret & Chottard, 1992). *sym-trans*-[Pt₂Cl₄(PBU₃⁺)₂] with dimethyl sulfide has been shown to give a compound with the formula [PtCl₂(PBU₃⁺)(SMe₂)] (Pidcock, Richards & Venanzi, 1966); a *cis* configuration has been suggested based on the fact that the complex is colorless and on the ¹J_{Pt-P} coupling constant of 3386 Hz. However, neither argument is strictly straightforward since the UV-visible absorption spectrum of a *trans*-PtCl₂PS chromophore is not known and the ¹J_{Pt-P} ranges for Pt—P bonds *trans* to S and *trans* to Cl overlap (Allen & Sze, 1971; Cetinkaya, Hitchcock, Lappert, Pye & Shaw, 1979; Anderson, Clark & Davies, 1981). The analogous reaction with di-*n*-butyl sulfide has therefore been carried out and the crystal structure of the product, *cis*-[PtCl₂(PBU₃⁺)(SBU₂⁺)] (I), determined.



Final positional parameters for the two independent molecules in the lattice are given in Table 1 and selected bond lengths and bond angles are listed in Table 2. Fig. 1 is an ORTEP (Johnson, 1965) drawing of molecule (1) and Fig. 2 shows the crystal packing.

The coordination of the platinum is square-planar, with maximum deviations from the least-squares

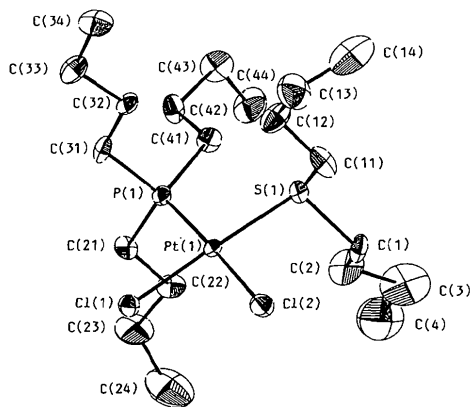


Fig. 1. ORTEP drawing of the title compound (30% ellipsoids) showing the numbering scheme.

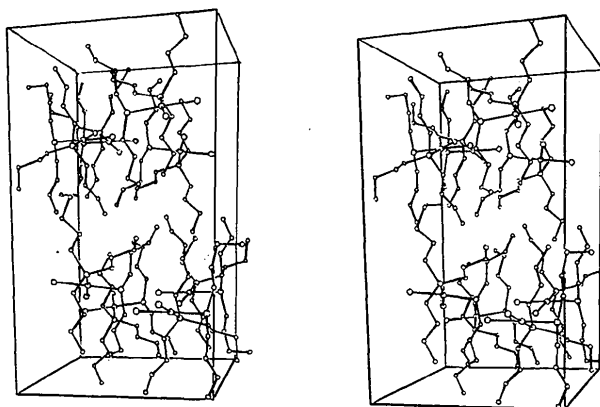


Fig. 2. Stereoview of the crystal packing.

planes through the atoms Pt(1), S(1), P(1), C(11), and C(12) of 0.012 Å [molecule (1)] and 0.016 Å [molecule (2)]. The phosphine and sulfide ligands are in the *cis* position. The Pt—P, Pt—S, and Pt—Cl bond lengths are as expected for a *cis*-PtCl₂PS chromophore (Huffman & Lloyd, 1989), with the Pt—Cl bond *trans* to P significantly longer than the Pt—Cl bond *trans* to S. There are no apparent intermolecular contacts.

Since the nucleophilic attack of di-*n*-butyl sulfide on *sym-trans*-[Pt₂Cl₄(PBU₃⁺)₂] initially yields, according to the large *trans* effect of the phosphine ligand, the complex *trans*-[PtCl₂(PBU₃⁺)(SBU₂⁺)], the present study shows that the latter species subsequently isomerizes to its *cis* analogue. Such an isomerization to the thermodynamically more stable *cis* configuration has been observed previously for other complexes of the type *cis*-[PtCl₂(PR₃)₂] (Cusumano, Guglielmo, Ricevuto, Sostero, Traverso & Kemp, 1981) and *cis*-[PtCl₂(PR₃)(SR₂)] (Anderson, Clark & Davies, 1981).

Experimental

Crystal data

C₂₀H₄₅Cl₂PPtS
M_r = 614.6
 Monoclinic
*P*2₁/*a*
a = 18.93 (1) Å
b = 23.029 (8) Å
c = 12.807 (4) Å
 β = 90.24 (4)°
V = 5584 (4) Å³
Z = 8
D_x = 1.46 Mg m⁻³

Mo *K*α radiation

λ = 0.7107 Å

Cell parameters from 25 reflections

θ = 10–11°

μ = 5.40 mm⁻¹

T = 291 K

Plate

0.7 × 0.4 × 0.3 mm

Colorless

Crystal source: ether/hexane solution

Data collection

Nonius CAD-4 diffractometer

*R*_{int} = 0.042

θ_{\max} = 22°

ω - 2θ scans $h = -19 \rightarrow 19$
 Absorption correction: $k = 0 \rightarrow 24$
 empirical $l = 0 \rightarrow 13$
 $T_{\min} = 0.85$, $T_{\max} = 1.08$ 2 standard reflections
 7479 measured reflections frequency: 120 min
 6816 independent reflections intensity variation: none
 2601 observed reflections
 $[I \geq 3\sigma(I)]$

Refinement

Refinement on F^2 $(\Delta/\sigma)_{\max} = 0.21$
 Final $R = 0.061$ $\Delta\rho_{\max} = 1.75 \text{ e } \text{\AA}^{-3}$
 $wR = 0.069$ $\Delta\rho_{\min} = -1.23 \text{ e } \text{\AA}^{-3}$
 2601 reflections Atomic scattering factors
 452 parameters from *International Tables*
 H atoms not introduced for *X-ray Crystallography*
 $w = 1$ (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Molecule (1)				
Pt(1)	-0.00799 (8)	0.23711 (6)	0.7983 (1)	0.0628
S(1)	-0.0325 (5)	0.2347 (5)	0.9718 (6)	0.0808
Cl(1)	0.0143 (6)	0.2389 (5)	0.6226 (7)	0.0968
Cl(2)	-0.1260 (5)	0.2647 (6)	0.7654 (7)	0.1049
P(1)	0.1054 (5)	0.2118 (4)	0.8196 (7)	0.0734
C(1)	-0.105 (1)	0.180 (1)	0.988 (3)	0.0924
C(2)	-0.071 (2)	0.120 (2)	0.976 (5)	0.0882
C(3)	-0.109 (4)	0.074 (2)	1.036 (5)	0.1734
C(4)	-0.083 (4)	0.019 (2)	0.988 (7)	0.3486
C(11)	-0.073 (2)	0.305 (1)	1.010 (3)	0.0906
C(12)	-0.021 (2)	0.356 (2)	0.991 (4)	0.1405
C(13)	-0.054 (3)	0.415 (2)	1.022 (5)	0.2294
C(14)	-0.072 (4)	0.414 (2)	1.138 (5)	0.1799
C(21)	0.132 (2)	0.150 (1)	0.734 (2)	0.0699
C(22)	0.089 (2)	0.095 (2)	0.759 (3)	0.0872
C(23)	0.112 (3)	0.051 (2)	0.677 (5)	0.1796
C(24)	0.053 (4)	0.007 (3)	0.659 (7)	0.2939
C(31)	0.166 (1)	0.272 (1)	0.786 (2)	0.0891
C(32)	0.149 (2)	0.325 (1)	0.852 (3)	0.0879
C(33)	0.200 (2)	0.373 (2)	0.815 (3)	0.1204
C(34)	0.187 (3)	0.428 (2)	0.880 (4)	0.1363
C(41)	0.128 (2)	0.191 (2)	0.957 (2)	0.0893
C(42)	0.205 (2)	0.169 (2)	0.967 (2)	0.1068
C(43)	0.219 (2)	0.148 (2)	1.082 (3)	0.1363
C(44)	0.193 (3)	0.086 (2)	1.094 (4)	0.1890
Molecule (2)				
Pt(1')	0.24684 (8)	0.29784 (8)	1.3032 (1)	0.0861
S(1')	0.2729 (6)	0.2830 (5)	1.4749 (7)	0.1059
Cl(1')	0.2225 (6)	0.3097 (6)	1.1271 (8)	0.1228
Cl(2')	0.3584 (6)	0.2596 (7)	1.2586 (9)	0.1470
P(1')	0.1400 (5)	0.3348 (5)	1.3326 (7)	0.0878
C(1')	0.308 (2)	0.206 (1)	1.486 (3)	0.0822
C(2')	0.254 (3)	0.163 (2)	1.440 (5)	0.2097
C(3')	0.274 (4)	0.101 (2)	1.472 (5)	0.2581
C(4')	0.334 (4)	0.083 (3)	1.402 (6)	0.2446
C(11')	0.352 (1)	0.327 (2)	1.506 (3)	0.1212
C(12')	0.331 (3)	0.391 (2)	1.516 (6)	0.2444
C(13')	0.377 (3)	0.417 (3)	1.603 (7)	0.2763
C(14')	0.332 (5)	0.463 (4)	1.655 (7)	0.3518
C(21')	0.123 (2)	0.353 (2)	1.472 (2)	0.0908
C(22')	0.050 (2)	0.382 (2)	1.491 (3)	0.1374
C(23')	0.049 (2)	0.403 (3)	1.607 (3)	0.1558
C(24')	-0.018 (3)	0.434 (3)	1.632 (5)	0.2581
C(31')	0.123 (2)	0.403 (1)	1.262 (2)	0.0869
C(32')	0.177 (2)	0.449 (2)	1.287 (3)	0.1114
C(33')	0.171 (4)	0.493 (2)	1.197 (3)	0.2225

C(34')	0.185 (5)	0.552 (2)	1.238 (6)	0.2778
C(41')	0.071 (2)	0.284 (1)	1.286 (3)	0.1093
C(42')	0.080 (2)	0.224 (2)	1.338 (3)	0.1040
C(43')	0.036 (3)	0.178 (2)	1.282 (4)	0.1967
C(44')	0.050 (3)	0.120 (2)	1.337 (5)	0.1814

Table 2. Selected bond lengths (\AA) and angles ($^\circ$)

Pt(1)—S(1)	2.272 (8)	Pt(1')—S(1')	2.28 (1)
Pt(1)—Cl(1)	2.292 (9)	Pt(1')—Cl(1')	2.32 (1)
Pt(1)—Cl(2)	2.360 (9)	Pt(1')—Cl(2')	2.36 (1)
Pt(1)—P(1)	2.241 (9)	Pt(1')—P(1')	2.23 (1)
S(1)—C(1)	1.87 (2)	S(1')—C(1')	1.89 (2)
S(1)—C(11)	1.86 (2)	S(1')—C(11')	1.84 (2)
P(1)—C(21)	1.86 (2)	P(1')—C(21')	1.86 (2)
P(1)—C(31)	1.84 (2)	P(1')—C(31')	1.84 (2)
P(1)—C(41)	1.87 (2)	P(1')—C(41')	1.85 (2)
Cl(1)—Pt(1)—S(1)	178.8 (4)	Cl(1')—Pt(1')—S(1')	177.9 (4)
Cl(2)—Pt(1)—S(1)	89.1 (3)	Cl(2')—Pt(1')—S(1')	89.3 (4)
Cl(2)—Pt(1)—Cl(1)	89.9 (4)	Cl(2')—Pt(1')—Cl(1')	89.0 (4)
P(1)—Pt(1)—S(1)	94.3 (3)	P(1')—Pt(1')—S(1')	95.0 (4)
P(1)—Pt(1)—Cl(1)	86.8 (3)	P(1')—Pt(1')—Cl(1')	86.7 (4)
P(1)—Pt(1)—Cl(2)	176.6 (3)	P(1')—Pt(1')—Cl(2')	175.7 (4)
C(1)—S(1)—Pt(1)	106.3 (12)	C(1')—S(1')—Pt(1')	106.6 (12)
C(11)—S(1)—Pt(1)	108.8 (12)	C(11')—S(1')—Pt(1')	107.4 (13)
C(11)—S(1)—C(1)	104.3 (15)	C(11')—S(1')—C(1')	102.3 (16)
C(21)—P(1)—Pt(1)	112.6 (11)	C(21')—P(1')—Pt(1')	113.8 (10)
C(31)—P(1)—Pt(1)	111.7 (11)	C(31')—P(1')—Pt(1')	113.9 (12)
C(31)—P(1)—C(21)	105.6 (14)	C(31')—P(1')—C(21')	104.5 (15)
C(41)—P(1)—Pt(1)	113.2 (9)	C(41')—P(1')—Pt(1')	110.3 (12)
C(41)—P(1)—C(21)	107.2 (15)	C(41')—P(1')—C(21')	109.0 (15)
C(41)—P(1)—C(31)	105.9 (14)	C(41')—P(1')—C(31')	104.8 (14)

The structure was solved by direct methods (Sheldrick, 1986). For the *n*-butyl groups, unrestrained refinements led to unreasonable bond lengths; accordingly, the P—C and S—C bond lengths were restrained to 1.83(3) \AA and the C—C bond lengths to 1.54(3) \AA and the X—C—C bond angles (X = C, P, S) to 109(3) $^\circ$. The least-squares refinements were carried out in three blocks.

We thank Professor J. C. Chottard for helpful discussions.

Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55664 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1017]

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