

1784 reflections
235 parameters
Idealized H-atom positions
riding on host atom
 $w = 1/[\sigma^2(F) + 0.0021F^2]$

Atomic scattering factors
from *International Tables
for X-ray Crystallography*
(1992, Vol. C, Tables
6.1.1.4 and 6.1.1.5)

Data collection: *P3/P4-PC* (Siemens, 1991). Cell refinement: *P3/P4-PC*. Data reduction: *XDISK* in *SHELXTL/PC* (Sheldrick, 1991). Program(s) used to solve structure: *XS* in *SHELXTL/PC*. Program(s) used to refine structure: *XLS* in *SHELXTL/PC*. Molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *XPUBL* in *SHELXTL/PC*.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Co1	0.0278 (1)	0.0560 (1)	0.5630 (1)	0.0035 (1)
Br1	0.1071 (1)	-0.0715 (1)	0.4654 (1)	0.0068 (1)
Br2	0.1679 (1)	0.1423 (1)	0.6486 (1)	0.0057 (1)
Si1	-0.1622 (2)	0.0314 (2)	0.7067 (2)	0.0037 (1)
N1	-0.1699 (7)	-0.1909 (6)	0.5850 (5)	0.0044 (3)
N2	-0.0694 (6)	0.1608 (6)	0.4892 (5)	0.0042 (3)
O1	-0.0831 (5)	-0.0170 (5)	0.6300 (4)	0.0041 (2)
C1	-0.0931 (10)	0.1145 (9)	0.4018 (7)	0.0066 (5)
C2	-0.0108 (10)	0.2606 (8)	0.4772 (8)	0.0064 (4)
C3	-0.1850 (8)	0.1777 (8)	0.5319 (7)	0.0045 (4)
C4	-0.1799 (8)	0.2322 (7)	0.6178 (6)	0.0037 (3)
C5	-0.1951 (9)	0.3406 (8)	0.6208 (8)	0.0053 (4)
C6	-0.1924 (9)	0.3932 (9)	0.6968 (9)	0.0059 (4)
C7	-0.1732 (10)	0.3444 (9)	0.7761 (9)	0.0063 (5)
C8	-0.1616 (9)	0.2362 (8)	0.7752 (7)	0.0049 (4)
C9	-0.1668 (8)	0.1785 (7)	0.6983 (7)	0.0043 (3)
C10	-0.3120 (8)	-0.0160 (8)	0.6881 (7)	0.0041 (3)
C11	-0.4029 (9)	0.0520 (9)	0.6995 (7)	0.0054 (4)
C12	-0.5150 (9)	0.0195 (12)	0.6878 (9)	0.0078 (6)
C13	-0.5378 (10)	-0.0779 (12)	0.6642 (10)	0.0085 (6)
C14	-0.4502 (9)	-0.1498 (11)	0.6515 (9)	0.0068 (5)
C15	-0.3384 (8)	-0.1213 (8)	0.6662 (7)	0.0047 (4)
C16	-0.2529 (9)	-0.2049 (8)	0.6591 (7)	0.0048 (4)
C17	-0.0906 (10)	-0.2809 (8)	0.5838 (9)	0.0070 (5)
C18	-0.2241 (10)	-0.1801 (9)	0.4981 (7)	0.0061 (4)
C19	-0.1138 (9)	-0.0099 (8)	0.8172 (6)	0.0053 (4)

Table 2. Selected geometric parameters (Å, °)

Co1—Br1	2.406 (2)	C3—C4	1.486 (14)
Co1—Br2	2.385 (2)	C4—C5	1.407 (13)
Co1—N2	2.100 (8)	C4—C9	1.416 (14)
Co1—O1	1.911 (6)	C5—C6	1.34 (2)
Si1—O1	1.623 (7)	C6—C7	1.38 (2)
Si1—C9	1.898 (10)	C7—C8	1.40 (2)
Si1—C10	1.898 (10)	C8—C9	1.39 (2)
Si1—C19	1.856 (10)	C10—C11	1.398 (14)
N1—C16	1.507 (14)	C10—C15	1.43 (2)
N1—C17	1.491 (14)	C11—C12	1.40 (2)
N1—C18	1.479 (14)	C12—C13	1.33 (2)
N2—C1	1.485 (14)	C13—C14	1.40 (2)
N2—C2	1.472 (14)	C14—C15	1.39 (2)
N2—C3	1.531 (12)	C15—C16	1.482 (14)
Br1—Co1—Br2	112.6 (1)	N2—C3—C4	113.9 (8)
Br1—Co1—N2	108.7 (2)	C3—C4—C5	119.4 (9)
Br2—Co1—N2	112.1 (2)	C3—C4—C9	122.5 (9)
Br1—Co1—O1	105.3 (2)	C5—C4—C9	118.0 (9)
Br2—Co1—O1	114.5 (2)	C4—C5—C6	121.7 (11)
N2—Co1—O1	103.0 (3)	C5—C6—C7	122.0 (11)
O1—Si1—C9	110.5 (4)	C6—C7—C8	117.4 (11)
O1—Si1—C10	108.0 (4)	C7—C8—C9	122.4 (10)
O1—Si1—C19	106.5 (4)	Si1—C9—C4	123.2 (8)
C9—Si1—C10	111.4 (4)	Si1—C9—C8	118.4 (8)
C9—Si1—C19	110.9 (5)	C4—C9—C8	118.4 (9)
C10—Si1—C19	109.4 (5)	Si1—C10—C11	120.0 (8)
C16—N1—C17	109.1 (8)	Si1—C10—C15	123.0 (7)
C16—N1—C18	113.5 (8)	C11—C10—C15	117.0 (9)
C17—N1—C18	109.6 (8)	C10—C11—C12	121.8 (11)
Co1—N2—C1	109.0 (6)	C11—C12—C13	120.4 (12)
Co1—N2—C2	111.6 (6)	C12—C13—C14	120.6 (12)
C1—N2—C2	109.1 (8)	C13—C14—C15	120.5 (12)
Co1—N2—C3	110.8 (6)	C10—C15—C14	119.7 (10)
C1—N2—C3	105.6 (8)	C10—C15—C16	123.7 (9)
C2—N2—C3	110.5 (8)	C14—C15—C16	116.6 (10)
Co1—O1—Si1	126.4 (4)	N1—C16—C15	114.4 (8)

The authors would like to thank Fundación Andes for the purchase of the single-crystal diffractometer currently operating at the Universidad de Chile.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, least-squares-planes data and complete geometry have been deposited with the IUCr (Reference: BK1030). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Dimer [PtCl₂{P(C₂H₅)₃}{(C₆H₅)SOCH₂}]₂

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Abstract

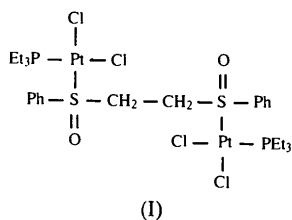
The structure determination of μ -[meso-1,2-bis(phenylsulfanyl)ethane-*S:S'*]bis[*cis*-dichloro(triethylphosphine)platinum(II)] revealed the occurrence of discrete dimers,

formed by two platinum complexes related by an inversion centre and connected by the ($-\text{CH}_2-\text{CH}_2-$) group attached to the S atoms, with the centre of the C—C bond [$\text{C}13-\text{C}13' = 1.54(1) \text{ \AA}$] located at the origin. The metal has a *cis*-square-planar coordination environment, and the geometries about the P and S atoms are tetrahedral.

Comment

Diastereoisomeric *meso* and *rac* forms of 1,2-bis(phenylsulfinyl)ethane can be separated readily. The *rac* isomer has a melting point (394–396 K) lower than the *meso* isomer (440–442 K), although the solid-state IR spectra are very similar (Filgueiras, Celso, Marques & Johnson, 1982). The ^1H NMR spectra allow the identification of the diastereoisomers. The *meso* isomer has equivalent $-\text{CH}_2-\text{CH}_2-$ protons and shows only a single resonance at 2.88 p.p.m., while the $-\text{CH}_2-\text{CH}_2-$ protons in the *rac* compound are non-equivalent, displaying a complex multiplet centred at about the same frequency (Cattalini, Michelson, Marangoni & Pelizzi, 1979).

The ^1H NMR spectrum of the title complex, (I), in CDCl_3 showed two virtual quartets occurring at 4.36 and 4.67 p.p.m. for the $-\text{CH}_2-\text{CH}_2-$ group, due to the two magnetically non-equivalent methylene protons at each C atom. However, the ^{31}P and ^{195}Pt NMR spectra indicated magnetically equivalent phosphorus and platinum nuclei.



The *meso*-(PhSOCH_2) $_2$ ligand can bind to different metal centres *via* either the O or S atoms. This ligand reacts with a soft Lewis acid, namely $\text{K}_2[\text{PtCl}_4]$, yielding the corresponding neutral platinum(II) complex, *cis*- $[\text{PtCl}_2\{\text{meso}-(\text{PhSOCH}_2)_2\}]$, in which the disulfoxide acts as a bidentate *S,S*-chelating ligand (Cattalini, Michelson, Marangoni & Pelizzi, 1979). On the other hand, the hard acid, Ph_3SnCl , forms a $\text{Ph}_3\text{SnCl}-(\text{PhSOCH}_2)$ complex (Filgueiras, Holland, Johnson & Raithby, 1982) which utilizes the O atoms.

The stereochemistry of some square-planar platinum complexes is dependent on electronic and/or steric forces (Meek, Nicpon & Meek, 1970). The *cis* arrangement of $\text{P}-\text{Pt}-\text{S}$ [$93.4(1)^\circ$] in the title compound can be rationalized by the necessity to reduce the competition between the P and S atoms for the *d* orbitals of the metal.

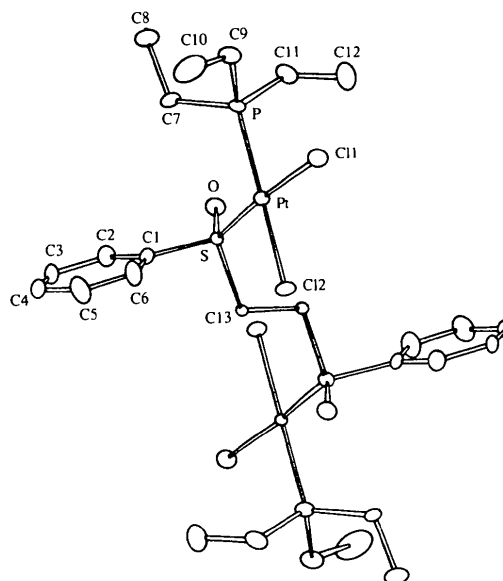


Fig. 1. An ORTEP (Johnson, 1965) view of the title dimer with numbering for the independent unit.

Experimental

To obtain the title compound, $[\text{PtCl}(\mu\text{-Cl})(\text{PEt}_3)]_2$ (0.10 g, 0.13 mmol) was dissolved in a small amount of hot C_6H_6 and treated with *meso*-(PhSOCH_2) $_2$ (0.26 g, 0.13 mmol) dissolved in the same solvent. The mixture was refluxed for 0.5 h and the product was filtered. White air-stable crystals (m.p. 448–449 K) were obtained by recrystallization from $\text{C}_6\text{H}_6/\text{CH}_2\text{Cl}_2$ (1:4). Elemental chemical analysis indicated 29.82% C and 4.20% H.

Crystal data

$[\text{Pt}_2\text{Cl}_4(\text{C}_{14}\text{H}_{14}\text{O}_2\text{S}_2)-$
 $(\text{C}_6\text{H}_{15}\text{P})_2]$

$M_r = 1046.7$

Orthorhombic

Pbca

$a = 12.835(3) \text{ \AA}$

$b = 17.596(3) \text{ \AA}$

$c = 16.015(3) \text{ \AA}$

$V = 3617(1) \text{ \AA}^3$

$Z = 4$

$D_x = 1.9222 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 21 reflections

$\theta = 9-13^\circ$

$\mu = 8.3277 \text{ mm}^{-1}$

$T = 298 \text{ K}$

Block

$0.4 \times 0.3 \times 0.2 \text{ mm}$

White

Data collection

Enraf-Nonius CAD-4 diffractometer

$\omega/2\theta$ scans

Absorption correction:

refined from ΔF

(DIFABS; Walker &

Stuart, 1983)

$T_{\min} = 0.05$, $T_{\max} = 0.19$

3900 measured reflections

2794 independent reflections

1889 observed reflections

$[F \geq 6\sigma(F)]$

$R_{\text{int}} = 0.0347$

$\theta_{\text{max}} = 25^\circ$

$h = 0 \rightarrow 15$

$k = 0 \rightarrow 20$

$l = 0 \rightarrow 18$

20 standard reflections

frequency: 60 min

intensity decay: 0.9%

Refinement

Refinement on <i>F</i>	(Δ/σ) _{max} = 0.01
<i>R</i> = 0.0383	$\Delta\rho_{\text{max}} = 1.57 \text{ e } \text{\AA}^{-3}$
<i>wR</i> = 0.0428	$\Delta\rho_{\text{min}} = -1.85 \text{ e } \text{\AA}^{-3}$
<i>S</i> = 0.89	Extinction correction: none
1906 reflections	Atomic scattering factors
181 parameters	from <i>International Tables</i>
Only coordinates of H atoms	for <i>X-ray Crystallography</i>
refined	(1974, Vol. IV)
$w = 1/[\sigma^2(F)$	
$+ 0.00637F^2]$	

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

$$B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j \text{ (Hamilton, 1959).}$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
Pt	0.20831 (3)	0.11835 (2)	0.03934 (3)	2.37 (2)
S	0.0516 (2)	0.0878 (2)	0.0861 (2)	2.47 (8)
P	0.1852 (3)	0.2443 (2)	0.0636 (2)	3.0 (1)
Cl1	0.3654 (3)	0.1468 (2)	-0.0225 (2)	4.4 (1)
Cl2	0.2508 (3)	-0.0104 (2)	0.0186 (2)	3.9 (1)
O	-0.0316 (7)	0.1434 (5)	0.0686 (5)	3.6 (3)
C1	0.054 (1)	0.0646 (6)	0.1944 (6)	2.9 (4)
C2	-0.035 (1)	0.0784 (7)	0.2388 (8)	4.2 (5)
C3	-0.036 (2)	0.0577 (8)	0.3240 (8)	4.9 (6)
C4	0.049 (1)	0.0245 (8)	0.3597 (8)	4.7 (5)
C5	0.135 (1)	0.0105 (9)	0.3115 (9)	5.5 (6)
C6	0.140 (1)	0.0304 (9)	0.2298 (9)	5.0 (6)
C7	0.100 (1)	0.2662 (6)	0.1508 (9)	4.7 (5)
C8	0.096 (2)	0.3486 (7)	0.179 (1)	6.1 (7)
C9	0.306 (1)	0.2938 (8)	0.089 (1)	4.5 (5)
Cl0	0.361 (2)	0.266 (1)	0.165 (1)	9. (1)
Cl11	0.129 (2)	0.2940 (8)	-0.0239 (9)	5.3 (6)
Cl12	0.179 (2)	0.282 (1)	-0.106 (1)	7.4 (8)
Cl13	0.008 (1)	-0.0024 (6)	0.0475 (6)	2.5 (3)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Pt—S	2.212 (3)	S—C1	1.78 (1)
Pt—P	2.270 (3)	S—C13	1.79 (1)
Pt—Cl11	2.302 (3)	P—C7	1.82 (1)
Pt—Cl12	2.353 (3)	P—C9	1.82 (1)
S—O	1.475 (9)	P—C11	1.80 (1)
S—Pt—P	93.4 (1)	Pt—S—O	115.6 (4)
S—Pt—Cl12	91.4 (1)	Pt—S—C13	112.4 (4)
Cl11—Pt—Cl12	86.9 (1)	Pt—S—C1	111.7 (4)
Cl11—Pt—P	88.6 (1)	O—S—C1	110.4 (5)
S—Pt—Cl11	174.3 (3)	O—S—C13	107.2 (5)
P—Pt—Cl12	173.9 (1)	Cl1—S—C13	97.9 (5)
Pt—P—C7	114.7 (4)	C7—P—C9	103.8 (7)
Pt—P—C9	113.2 (5)	C7—P—C11	104.7 (7)
Pt—P—Cl11	113.1 (5)	C9—P—C11	106.4 (7)

The structure was solved by analysis of the Patterson map (*SHELXS86*; Sheldrick, 1985) followed by difference Fourier syntheses and refinement using *SHELX76* (Sheldrick, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1113). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Redetermination of Bis(*N,N*-diethyldithiocarbamato)nickel(II)

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Abstract

The crystal structure of the α form of bis(*N,N*-diethyldithiocarbamato-*S,S'*)nickel(II), [Ni(C₅H₁₀NS₂)₂], has been redetermined at 290 K by single-crystal X-ray methods. The Ni atom assumes a four-coordinate square-planar geometry with two isobidentate dithiocarbamate groups. The results confirm those of a previous study [Bonamico, Dessy, Mariani, Vaciego & Zambonelli (1965). *Acta Cryst.* **19**, 619–627] but are more precise.

Comment

The structure and chemistry of nickel(II) dithiocarbamates continue to be of interest. Three forms of bis(*N,N*-diethyldithiocarbamato)nickel(II) have been reported (Bonamico, Dessy, Mariani, Vaciego & Zambonelli, 1965; Khan, Nazrul, Fackler, Murray & Heinrich, 1987). The structure of the α form, (I), was determined (Bonamico *et al.*, 1965) by photographic methods using Cu *K* α radiation to a final *R* factor of only 0.10.