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(η^3-Allyl-2κ^3C)(chloro-1κCl)(μ-*N*,*N*′-diethyldithioxamidato-1:2κ^4S,S':*N*,*N*′)-[diphenyl(2-pyridyl)phosphine-1κP]-palladium(II)platinum(II) chloroform solvate

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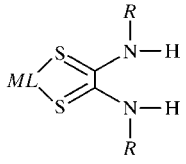
The title compound, $[PdPtCl(C_3H_5)(C_6H_{10}N_2S_2)(C_{17}H_{14}NP)]\cdot CHCl_3$, was obtained by deprotonation of the initial platinum(II) complex of the dithioxamide and subsequent reaction with $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$. Both metal atoms exhibit a square-planar coordination geometry, with the two planes forming a dihedral angle of 21.7 (2)°. The dithioxamide bis-chelating bridge is flat.

Comment

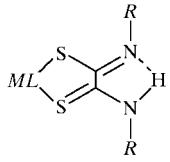
Secondary dithioxamides, $H_2R_2C_2N_2S_2$ (*R* is an alkyl group), are effective chelating ligands and readily afford *S*,*S*′-coordinated metal complexes, such as (I) in the *Scheme* (Antolini *et al.*, 1987; Desseyn *et al.*, 1978; Rosace *et al.*, 1993). One of the two amidic H atoms in (I) can easily be removed and monometallic complexes, such as (II), are obtained, in which the dithioxamide (DTO) chelate is in an imidothiolic form (Lanza *et al.*, 1994). Removal of the residual amidic H atom in (II) transforms the coordinated dithioxamide to a diimidothiolic binucleating ligand, as in (III).

As a consequence of these reaction possibilities, secondary dithioxamides can be exploited as binucleating ligands suitable for the sterically and topologically controlled synthesis of oligonuclear metal complexes (Lanza *et al.*, 1996, 2000). We have evidence that steric hindrance on N and nitrogen basicity in complexes like (II) are important factors in determining the reactivity of the N—H···N frame. For this reason, it is useful to collect structural information on *R* substituents, with regard to both their steric congestion and their electronic influence over the N—C—S fragment. Hence, the title compound, (IV), has been crystallized and its structure is presented here.

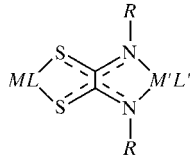
Compound (IV) is a palladium–platinum example of (III) and was obtained through the deprotonation of the corresponding Pt^{II} form of (I). In the solid state, the complex is packed with chloroform solvate molecules in a 1:1 ratio. We have attempted to obtain unsolvated crystals, but the X-ray diffraction data were not of sufficient quality to obtain an



(I)



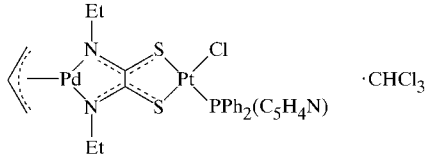
(II)



(III)

M and *M*′ = transition metals
L and *L*′ = neutral or anionic ligands
R = alkyl group

acceptable refined model [orthorhombic, *Pbcm*, *a* = 11.689 (3), *b* = 22.362 (6) and *c* = 12.771 (6) Å, refined up to R_1(obs/all) = 0.0614/0.1033, with *S*(obs/all) = 0.896/0.895], mainly due to strong pseudosymmetry effects generated by the intersection of the complex unit with a crystallographic mirror plane. Despite the different crystal packing, the two complexes showed no significant differences, so no further efforts were made to obtain better samples of and diffraction data for the unsolvated solid. The occurrence of the two binuclear units might be explained by the sufficiently rigid skeleton of the complex and by the absence of significant intermolecular interactions in both crystal packings. The shortest distance from $CHCl_3$ is represented by the long contact of one DTO ethyl H atom with one Cl atom (H4*B*···Cl2 = 2.93 Å), and this is not strong enough to reduce the disorder of the free cocrystallized chloroform, whose geometry refinement thus had to be restrained.



(IV)

By considering the allyl as a 'short-bite' chelating ligand, both d^8 metal atoms exhibit the usual square-planar coordination. The Pd geometry appears quite distorted, as evidenced by the two opposite chelating angles, C—Pd—C and N—Pd—N, being much narrower than the two adjacent N—Pd—C angles, which are much larger than the expected value of 90° (Table 1). The central allyl atom, C8, is split over two almost symmetrical positions with respect to the coordination mean plane [50% occupancy, deviating by 0.48 (4) and −0.53 (4) Å,

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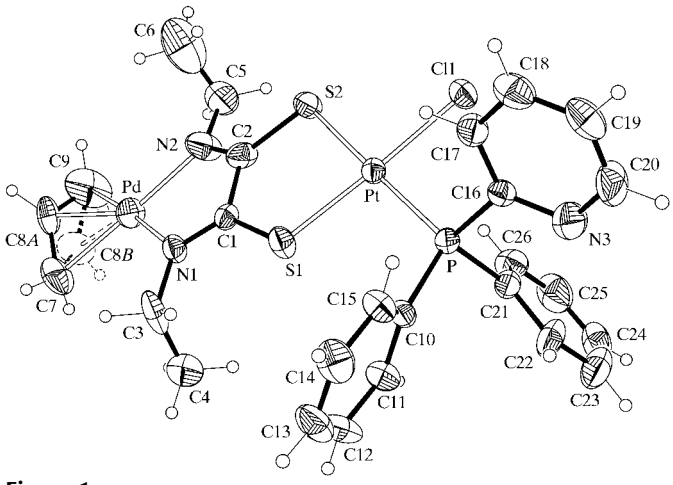

Figure 1
A perspective view of (IV), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines and atoms represent the alternative arrangement of the disordered allyl ligand. The disordered solvent chloroform molecule has been omitted for clarity.

respectively], as is usually observed in similar complexes, *e.g.* in our previous work on the related complex [(η^3-allyl)Pd-(μ-dibenzyl-DTO *N*,*N*′-Pd *S*,*S*′-Pt)Pt(PN)Cl] [PN is diphenyl-(2-pyridyl)phosphine; Lanza *et al.*, 2000].

The large size of the diphenyl(2-pyridyl)phosphine ligand has no significant influence on the Pt^{II} geometry because it can easily be accommodated in the coordination shell, avoiding significant steric hindrances. The fact that the deformation of the regular arrangement is only slight in (IV) is evidenced by the Pt bond angles being very close to the expected value of 90° and the four Pt bonds being of very similar length [to within 0.077 (3) Å]. However, there is a noticeable difference [0.059 (3) Å] between the two Pt—S distances, due to the different *trans* effects of the opposite ligands. This moiety is almost exactly equivalent to the same fragment we have previously reported in the related dibenzyl Pd–Pt complex and in another analogous compound, [(η^6-*p*-cymene)RuCl{μ-bis(2-hydroxypropyl)-DTO *N*,*N*′-Ru *S*,*S*′-Pt}Pt(PN)Cl] (Lanza *et al.*, 1996).

The Pd^{II} and Pt^{II} centres lie on the corresponding mean plane of the four bonded atoms [respective deviations of 0.034 (1) and 0.038 (1) Å], with a dihedral angle of 21.7 (2)°. The two coordination planes form angles of 6.2 (2) and 16.6 (1)° with the DTO bis-chelating bridge, and the metals deviate by 0.110 (1) and 0.430 (1) Å, respectively, on the same side. Therefore, (IV) is not perfectly planar. The Pt moiety is bent by 16.8 (1)° at the S···S bite, while the Pd fragment lies almost on the dithioxamidate plane. This difference is confirmed by the puckering analysis (Cremer & Pople, 1975) of the corresponding five-membered chelate rings, Pd/N1/C1/C2/N2 and Pt/S1/C1/C2/S2 [φ = 53 (12) and 169 (2)°, and Q = 0.040 (1) and 0.231 (4) Å, respectively], evidencing the significantly flatter coordination of the Pd centre, while both conformations are intermediate between half-chair and envelope.

Experimental

Diethyl dithioxamide was synthesized according to the method of Hurd *et al.* (1961). The title complex was prepared according to the following three-step procedure.

Step 1: *cis*-[$Pt(Me_2SO)(PN)Cl_2$] {1 mmol, prepared *in situ* by mixing equimolar quantities of *cis*-[$Pt(Me_2SO)_2Cl_2$] and PN}, in a minimum amount of chloroform (about 10 ml), was reacted with a stoichiometric amount of $H_2Et_2N_2C_2S_2$. The solution turned red and was allowed to stand at room temperature for 30 min. After this time, petroleum ether (313–333 K, about 50 ml) was added to the concentrated solution. The {[(PN)ClPt($H_2Et_2N_2C_2S_2$)]$^+$·Cl^-} salt precipitated immediately as a magenta powder, which was separated from the colourless supernatant and air dried. Yields were higher than 90%.

Step 2: sodium bicarbonate (200 mg) was added to 1 mmol of the salt prepared in step 1 dissolved in a minimum amount of chloroform (about 20 ml). The magenta solution immediately turned orange; after 30 min of stirring, the sodium bicarbonate was removed by filtration and the orange solution was concentrated to a small volume (about 1 ml). [(PN)ClPt($HEt_2N_2C_2S_2$)] precipitated as an orange powder, and was collected and air dried. Yields were higher than 90%.

Step 3: [$Pd(\eta^3$-$C_3H_5)(\mu$-$Cl)]_2$ (1 mmol) was dissolved in a 70:30 (*v*/*v*) chloroform–methanol mixture (about 30 ml) and reacted with half the molar equivalent of the [(PN)ClPt($HEt_2N_2S_2C_2$)] complex. The solution, which turned deep red, was allowed to stand for 2 h. The solvent was removed and the crude products, redissolved in a minimum amount of chloroform (about 10 ml), were placed on an alumina column and equilibrated with light petroleum. The desired product was collected as an orange eluate and concentrated to a small volume (about 1 ml). On adding petroleum ether (313–333 K, about 30 ml), the title bimetallic complex, (IV), precipitated as an orange powder. Yields were higher than 80%. The complex was then crystallized from a chloroform solution to obtain samples suitable for X-ray diffraction studies.

Spectroscopic analysis: ^{1}H NMR (300.13 MHz, $CDCl_3$, δ, p.p.m): 8.68 (*m*, 1H, py-H6), 8.47 (*m*, 1H, py-H3), 7.80–7.13, (22H, Ar-H and py-H), 5.39 (*m*, 1H, allyl CH), 4.81 (*dq*, $^2J_{HH}$ = 13.8 Hz, $^3J_{HH}$ = 6.8 Hz, 2H, N-CH_2- *cis* to P, part *AB* of *ABC*$_3$), 3.38 (*dq*, $^2J_{HH}$ = 13.8 Hz, $^3J_{HH}$ = 6.8 Hz, 2H, N-CH_2- *trans* to P, part *AB* of *ABC*$_3$), 1.15 (*t*, $^3J_{HH}$ = 6.8 Hz, 3H, N-CH_2CH_3 *trans* to P, part C_3 of *ABC*$_3$), 0.95 (*t*, $^3J_{HH}$ = 6.8 Hz, 3H, N-CH_2CH_3 *cis* to P, part C_3 of *ABC*$_3$), 5.42 (*m*, 1H, allyl central CH), 3.52 (*m*, $^3J_{HH}$ = 6.9 Hz, 1H, *syn*-allyl CH H), 3.50 (*m*, $^3J_{HH}$ = 6.9 Hz, 1H, *syn*-allyl CH H), 2.91 (*m*, $^3J_{HH}$ = 12.7 Hz, 1H, *anti*-allyl CH H), 2.89 (*m*, $^3J_{HH}$ = 12.7 Hz, 1H, *anti*-allyl CH H); ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$, δ, p.p.m.): 190.8 (*d*, $^3J_{CP}$ = 11 Hz, 1C, CS *trans* to P), 190.3 (*d*, $^3J_{CP}$ = 2 Hz, 1C, CS *cis* to P), 154.6–124.3 (17C, Ar-C), 52.8 (1C, N-CH_2), 52.1 (1C, N-CH_2), 13.0 (1C, N-CH_2CH_3), 12.7 (1C, N-CH_2CH_3), 115.5 (1C, allyl central CH), 58.0 (1C, allyl CH_2), 57.9 (1C, allyl CH_2); ^{31}P{^{1}H} NMR (121.49 MHz, $CDCl_3$, δ, p.p.m.): 17.3 (Pt—P, $^1J_{PtP}$ = 3267 Hz). Analysis calculated for $C_{26}H_{29}ClN_3PPdPtS_2$: C 38.33, H 3.59, N 5.16, S 7.83, Cl 4.30%; found: C 38.61, H 3.71, N 5.25, S 8.05, Cl 4.52%.

Crystal data

[$PdPtCl(C_3H_5)(C_6H_{10}N_2S_2)$-($C_{17}H_{14}NP$)]·$CHCl_3$
M_r = 934.92
Monoclinic, $P2_1/c$
a = 13.423 (3) Å
b = 13.561 (3) Å
c = 19.156 (4) Å
β = 106.83 (3)°
V = 3337 (1) Å^3
Z = 4
D_x = 1.861 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 50 reflections
θ = 6.3–15.0°
μ = 5.24 mm^{-1}
T = 298 (2) K
Irregular, orange
0.33 × 0.25 × 0.15 mm

Table 1
Selected geometric parameters (Å, °).

Pt—P	2.256 (2)	S1—C1	1.722 (7)
Pt—S1	2.258 (2)	S2—C2	1.716 (9)
Pt—S2	2.317 (2)	N1—C1	1.270 (8)
Pt—Cl1	2.333 (2)	N1—C3	1.461 (10)
Pd—N1	2.071 (6)	N2—C2	1.291 (9)
Pd—N2	2.079 (7)	N2—C5	1.650 (13)
Pd—C7	2.094 (10)	C1—C2	1.505 (10)
Pd—C9	2.073 (10)		
P—Pt—S1	92.65 (7)	N1—C1—C2	116.1 (7)
S1—Pt—S2	89.23 (7)	N1—C1—S1	124.6 (6)
P—Pt—Cl1	90.35 (7)	C2—C1—S1	119.3 (6)
S2—Pt—Cl1	87.78 (7)	N2—C2—C1	114.8 (7)
N1—Pd—N2	77.8 (3)	N2—C2—S2	125.0 (7)
C9—Pd—N2	106.3 (4)	C1—C2—S2	120.2 (6)
N1—Pd—C7	106.8 (4)		
C3—N1—C1—S1	0 (1)	S1—C1—C2—N2	173.8 (7)
C5—N2—C2—S2	15 (1)	N1—C1—C2—S2	176.0 (6)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4B···Cl2	0.96	2.93	3.515 (12)	120
C18—H18···Cl1^{i}	0.93	2.90	3.800 (11)	163

Symmetry code: (i) $1-x, 1-y, 1-z$.

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: ψ scan (Kopfmann & Huber, 1968)
$T_{min} = 0.249$, $T_{max} = 0.456$
7636 measured reflections
7328 independent reflections
3944 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 27.1°$
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 17$
$l = -24 \rightarrow 23$
3 standard reflections
every 197 reflections
intensity decay: 10%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.089$
$S = 0.80$
7328 reflections
361 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0424P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.20$ e Å^{-3}
$\Delta\rho_{min} = -0.82$ e Å^{-3}

Reflection intensities were evaluated by profile fitting of a 96-step peak scan of 2θ shells (Diamond, 1969). H atoms were located in idealized positions (C—H = 0.93–0.98 Å) and allowed to ride on their parent C atoms, with isotropic displacement parameters related to the refined values of their corresponding parent atoms. The allyl ligand appeared disordered and the middle C atom was split over two positions, each with 50% occupancy. The terminal methyl group of both *N*-ethyl substituents and the cocrystallized chloroform molecule were affected by a slight disorder, and it was necessary to restrain their displacement parameters during the model refinement.

Data collection: *P*3/*V* (Siemens, 1989); cell refinement: *P*3/*V*; data reduction: *SHELXTL-Plus* (Siemens, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XPW* in *SHELXTL* (Siemens, 1996); software used to prepare material for publication: locally modified *PARST*95 (Nardelli, 1995) and *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1566). Services for accessing these data are described at the back of the journal.

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