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cis-Bis(phenoxyacetato-*O*)bis(triphenylphosphine-*P*)platinum(II) dichloromethane solvate

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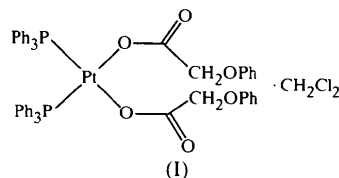
Abstract

The title complex, [Pt(C₈H₇O₃)₂(C₁₈H₁₅P)₂].CH₂Cl₂, has carboxylate ligands bonded in a monodentate manner.

Comment

We have been investigating silver(I) oxide-mediated reactions of carboxylic acids with platinum group metal halide complexes as a route to four-membered-ring metallalactone complexes of type *L*₂*M*{CHRC(O)O}. The product is dependent on the nature of the carboxylic acid; PhSO₂CH₂CO₂H gives the platinalactone complex [Pt{CH(SO₂Ph)C(O)O}(PPh₃)₂], whereas NCCH₂-CO₂H gives the bis(cyanomethyl) complex *cis*-[Pt(CH₂-CN)₂(PPh₃)₂], which has been characterized by X-ray crystallography (Henderson & Oliver, 1999). This paper describes the structure of the product formed in the

case of phenoxyacetic acid, *i.e.* *cis*-[Pt(O₂CCH₂OPh)₂(PPh₃)₂].CH₂Cl₂, (I).



Carboxylate ligands predominantly adopt a chelating or a bridging mode (Oldham, 1987), and when two carboxylate ligands are in a *cis* conformation, they tend to be of the latter type, often bridging several metal centres. Tan *et al.* (1996) isolated and characterized several short-chain platinum(II) carboxylic acid derivatives, which adopted a monodentate bonding mode. The title complex also demonstrates this monodentate bonding mode. One notable difference between the previously reported crystal structures of *cis*-carboxylatoplatinum(II) complexes and that presented here is the ancillary ligands. In the reported crystal structures of the complexes *cis*-[Pt(O₂CR)₂L₂] [*R* = Me or Ph, L₂ = Fe(C₅H₄PPh₂)₂ (dppf); *R* = CF₃, L₂ = Ph₂PCH₂PPh₂ (dppm)], chelating phosphines were employed, forcing a *cis* arrangement of the acetate ligands (Tan *et al.*, 1996).

The coordination around the platinum centre of *cis*-[Pt(O₂CCH₂OPh)₂(PPh₃)₂] is a distorted square plane as a result of the steric bulk of the triphenylphosphine and phenoxyacetate ligands. Thus, the P1—Pt—P2 angle [98.00 (6)°] is more obtuse than the O1—Pt—P1 angle [85.54 (15)°]. The remaining two bond angles are closer to ideal [O11—Pt—O1 87.75 (19) and O11—Pt—P2 89.93 (14)°]. The phenoxyacetate ligands are distorted out of the plane around the Pt atom. The O1 atom lies 0.433 (6) Å above the plane defined by atoms P1, P2 and Pt, while O11 is 0.178 (5) Å below this plane. This distortion is also reflected in the bond angles of the atoms *trans* to the O atoms [167.53 (16) and 170.64 (14)° for O1—Pt—P2 and O11—Pt—P1, respectively] with respect to an ideal value of 180°. The Pt—O bond lengths [2.082 (5) and 2.056 (4) Å for Pt—O1 and Pt—O11, respectively] are within the ranges of the platinum(II) carboxylate complexes described previously, *i.e.* *cis*-[Pt(O₂CR)₂L₂] [*R* = Me or Ph, L₂ = dppf; *R* = CF₃, L₂ = dppm; 2.034 (6)–2.089 (6) Å; Tan *et al.*, 1996]. The Pt—P bond lengths are not unusual.

The geometry of the carboxylate ligands with respect to one another is an *anti* arrangement of the carbonyl ligands [O2—C1—C11—O12 177.9 (6)°]. This geometry has been observed in the other reported *cis*-acetatoplatinum(II) complexes (Tan *et al.*, 1996). The O1—C1 bond distance is 1.177 (9) Å, fractionally shorter than that of O2—C1 [1.225 (9) Å], where O1 is the oxygen coordinated to the platinum. The other coordinating oxygen (O11) shows more single-bond charac-

ter, with an O—C distance of 1.285 (8) Å, and is comparable to previously reported bond lengths [1.257 (8)–1.298 (5) Å; Tan *et al.*, 1996].

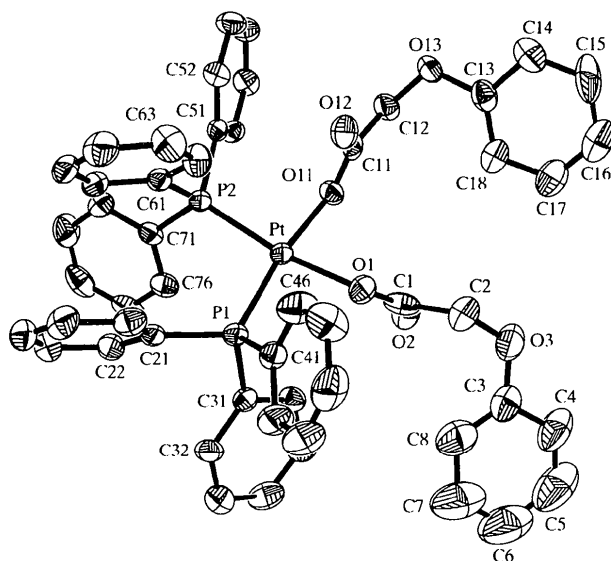


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. The solvate of crystallization and the H atoms have been omitted for clarity.

Experimental

[Pt(O₂CCH₂OPh)₂(COD)] (COD is 1,5-cyclooctadiene) was synthesized by refluxing a mixture of [PtCl₂(COD)] (0.097 g, 0.258 mmol), phenoxyacetic acid (0.081 g, 0.503 mmol) and silver(I) oxide (0.233 g, excess) in dichloromethane (20 ml) for 3 h. Silver salts were removed by filtration affording a deep-brown solution. The solvent was removed under vacuum and petroleum spirit was added producing a tan precipitate (0.065 g, 55%). *cis*-[Pt(O₂CCH₂OPh)₂(PPh₃)₂] was prepared by ligand displacement of COD from [Pt(O₂CCH₂OPh)₂(COD)] (0.045 g, 0.117 mmol) by triphenylphosphine (0.065 g, 0.247 mmol) in dichloromethane. Recrystallization by vapour diffusion of diethyl ether into a dichloromethane solution gave colourless tablets of an acceptable size. ³¹P NMR: δ 15.48 (¹J_{Pt-P} = 4084 Hz); ¹H NMR: δ 7.7–6.6 (*m*, Ph), 1.65 (*s*, CH₂).

Crystal data

[Pt(C₈H₇O₃)₂(C₁₈H₁₅P)₂].·
CH₂Cl₂

M_r = 1106.83

Monoclinic

*P*2₁/*c*

a = 11.4782 (1) Å

b = 17.9393 (3) Å

c = 23.3995 (2) Å

β = 101.006 (1)°

V = 4729.59 (10) Å³

Z = 4

D_x = 1.554 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 5533 reflections

θ = 1.44–26.45°

μ = 3.198 mm⁻¹

T = 203 (2) K

Tablet

0.25 × 0.23 × 0.08 mm

Colourless

Data collection

Siemens SMART CCD
diffractometer

Multi-scan

Absorption correction:

empirical (Blessing, 1995)

T_{min} = 0.671, *T_{max}* = 0.815

26 767 measured reflections

8799 independent reflections

6623 reflections with

I > 2σ(*I*)

R_{int} = 0.045

θ_{max} = 26.45°

h = −14 → 14

k = 0 → 22

l = 0 → 22

Intensity decay: none

Refinement

Refinement on *F*²

R [*F*² > 2σ(*F*²)] = 0.048

wR(*F*²) = 0.119

S = 1.065

8799 reflections

562 parameters

H atoms constrained

w = 1/[σ²(*F_o*²) + (0.0463*P*)²

+ 21.2066*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.009

Δρ_{max} = 1.779 e Å⁻³

Δρ_{min} = −1.380 e Å⁻³

Extinction correction: none

Scattering factors from

*International Tables for
Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Pt—O11	2.056 (4)	O1—C1	1.177 (9)
Pt—O1	2.082 (5)	O2—C1	1.225 (9)
Pt—P2	2.2305 (17)	O3—C3	1.369 (11)
Pt—P1	2.2501 (18)	O3—C2	1.396 (10)
P1—C31	1.812 (7)	O11—C11	1.285 (8)
P1—C41	1.829 (7)	O12—C11	1.234 (9)
P1—C21	1.830 (7)	O13—C13	1.385 (9)
P2—C61	1.820 (7)	O13—C12	1.414 (8)
P2—C71	1.825 (7)	C1—C2	1.597 (11)
P2—C51	1.833 (6)	C11—C12	1.510 (10)
O11—Pt—O1	87.75 (19)	O1—C1—C2	109.8 (6)
O11—Pt—P2	89.93 (14)	O2—C1—C2	115.9 (8)
O1—Pt—P2	167.53 (16)	O3—C2—C1	116.0 (7)
O11—Pt—P1	170.64 (14)	O3—C3—C8	124.7 (9)
O1—Pt—P1	85.54 (15)	O3—C3—C4	115.0 (10)
P2—Pt—P1	98.00 (6)	O12—C11—O11	125.3 (7)
C1—O1—Pt	124.6 (6)	O12—C11—C12	121.9 (7)
C3—O3—C2	117.2 (7)	O11—C11—C12	112.7 (7)
C11—O11—Pt	118.5 (4)	O13—C12—C11	114.5 (6)
C13—O13—C12	116.7 (6)	C18—C13—O13	124.4 (7)
O1—C1—O2	134.3 (9)	C14—C13—O13	115.2 (7)

H atoms were included in idealized positions riding on the atom to which they were bonded, with displacement parameters fixed at 1.2 times that of the parent atom. The maximum residual peak is 0.86 Å from the Pt atom and the minimum residual peak is 0.67 Å from the C11 atom.

Data collection: *SMART* (Siemens, 1994a). Cell refinement: *SAINT* (Siemens, 1994a). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997b). Molecular graphics: *SHELXTL* (Siemens, 1994b). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1245). Services for accessing these data are described at the back of the journal.

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Bis[1-hydroxy-3-methylpyridine-2(1*H*)-thionato-*O,S*]nickel(II)

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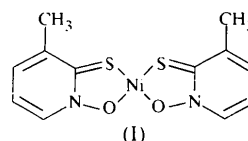
Abstract

In the structure of the title compound, [Ni(C₆H₆NOS)₂], the Ni atom is coordinated by a slightly distorted planar array of two S and two O atoms. The two 1-hydroxy-3-methylpyridine-2(1*H*)-thione (3-Me-HPT) ligands adopt a *cis* configuration. The average Ni—O and Ni—S bond lengths are 1.868 (2) and 2.130 (1) Å, respectively.

Comment

Owing to their useful bactericidal and antifungal activities, transition metal complexes of 1-hydroxypyridine-2(1*H*)-thione (HPT) have been widely investigated. Moreover, HPT exhibits unusual versatility in coordi-

nating to metals (Barnett *et al.*, 1977; West *et al.*, 1988). On the other hand, the simulation of many metallo-enzymes involving the thiolate group has also received considerable attention, particularly the assessment of the antitumor activity of some nickel complexes with chelating ligands (West *et al.*, 1993). As part of our studies of metal complexes of HPT (Xiong *et al.*, 1996; Song *et al.*, 1996), we now report the crystal structure of bis[1-hydroxy-3-methylpyridine-2(1*H*)-thionato-*O,S*]nickel(II), (I).



The complex is formed with *cis*-oriented 1-hydroxy-3-methylpyridine-2(1*H*)-thione (3-Me-HPT) ligands and shows nearly planar geometry. The Ni atom is coordinated by the S and O atoms of the two ligands and has a distorted square-planar geometry. The whole molecule exhibits a pseudo-*C*_{2v} symmetry, with the *C*₂ axis passing through the Ni atom and the midpoints of S1—S2 and O1—O2. When comparing the title compound with the analogue [Ni(PT)₂] (Chen *et al.*, 1991), the Ni—S and Ni—O bond distances in the two complexes are essentially the same within experimental error. However, the C—S bond lengths in (I) [average 1.728 (3) Å] are significant longer than those in the latter (average 1.710 Å) and the N—O bond lengths [average 1.320 (4) Å] are somewhat shorter than those in the latter (average 1.350 Å), which may be the result of steric hindrance of the 3-methyl group. The two O—Ni—S bite angles are nearly equal and close to 90°, as is found in [Ni(PT)₂], where PT is pyridine-2-thione. In the title complex, the two five-membered chelate rings are nearly planar, with maximum deviations of 0.024 (4) Å for C1 and 0.021 (4) Å for C11. The dihedral angle between these two planes is 5.3 (1)°. The complete molecule is almost planar. The Ni atom deviates by 0.002 (1) Å from the basal plane formed by the

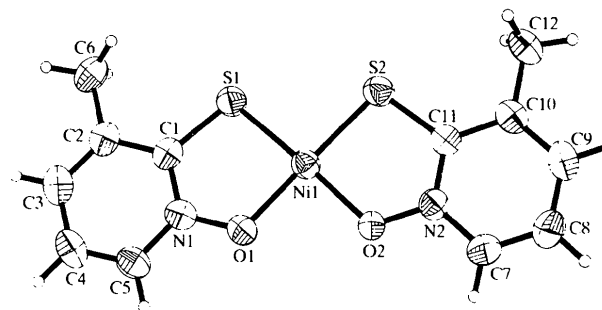


Fig. 1. A displacement ellipsoid plot (50% probability level) of the title molecule showing the atom-numbering scheme.