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trans-Diiodobis(triphenylarsine-*As*)-platinum(II)

Stefanus Otto and Andreas Roodt

Department of Chemistry, University of the Orange Free State, Bloemfontein 9300, South Africa. E-mail: char@uovsvm1.uovs.ac.za

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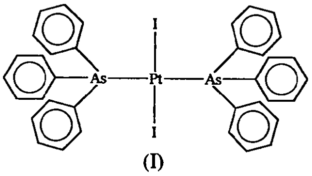
Abstract

The title compound, $[PtI_2\{As(C_6H_5)_3\}_2]$, is one of a few bis-As$X_3$ (X is alkyl or aryl) platinum(II) complexes isolated to date. It exhibits long Pt—As and Pt—I bonds. The difference between the two independent coordination units in the unit cell is a result of packing effects.

Comment

The title compound, *trans*-$[PtI_2(AsPh_3)_2]$, (I), is another structure in the series of rare bis-tertiary arsine complexes of platinum(II) (Otto, Roodt & Leipoldt, 1995; Otto & Roodt, 1996; Watkins, 1970). The complex crystallizes in space group $P\bar{1}$ with two independent molecules per asymmetric unit and with the Pt atoms on centres of symmetry. A square-planar geometry is exhibited, with a slight deviation in the As—Pt—I bond angles from 90°. The deviation from normal tetrahedral angle values in the $AsPh_3$ moiety is an indication of the large steric demand of this ligand.



(I)

The two independent coordination units (Fig. 1) differ significantly, especially in the torsion angles formed by the phenyl rings relative to the coordination plane (Table 1). There is also a difference in the I—Pt—As bond angles; 88.07 (6) and 91.93 (6)° for molecule 1 compared with 87.49 (5) and 92.51 (5)° for molecule 2. These differences are due to packing effects since there is no chemical difference between the two complexes. The different packing modes observed are illustrated in more detail in Table 2 and Fig. 2, including the significant differences in the phenyl-ring least-squares planes relative to the square-planar moiety.

Attempted reduction of the asymmetric unit to a single platinum moiety by placement in a non-special position or reduction of the unit call to $P1$ was unsuccessful, yielding an R value of >25%, in correlation with the significant differences in the two molecules.

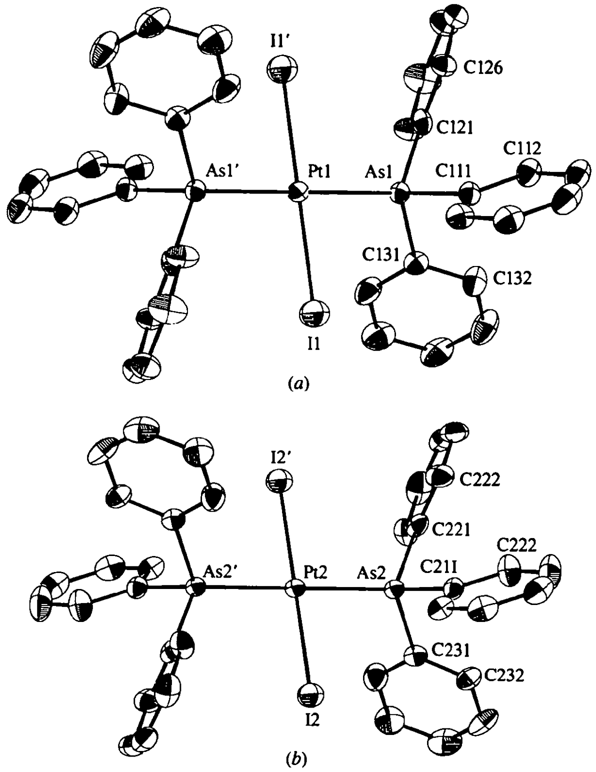


Fig. 1. The molecular structure of the title complex showing the numbering schemes and displacement ellipsoids (30% probability) of molecules 1 and 2 in (*a*) and (*b*), respectively. H atoms have been omitted for clarity. The phenyl rings are numbered with the first digit referring to the molecule (1 or 2), the second to the ring number (1–3) and the third to the atom number in the ring (1–6) (primed atoms are generated by the centre of symmetry).

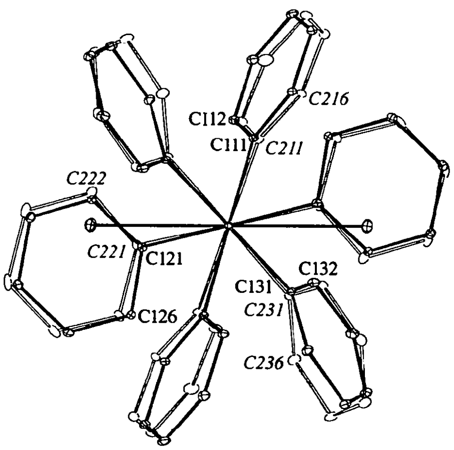


Fig. 2. The title structure showing the two independent molecules superimposed in order to illustrate the difference in the phenyl-ring orientations on account of the packing effects. The view is along the As—Pt—As axis. Solid bonds indicate molecule 1 and open bonds molecule 2.

Large average bond lengths of 2.404 (2) and 2.631 (2) Å are observed for the Pt—As and Pt—I bonds, respectively. The Pt—I lengths represent some of the longest determined to date compared with the following analogous phosphine complexes: *trans*-$[PtI_2(PMe_3)_2]$ 2.599 (2) Å (Hitchcock, Jacobson & Pidcock, 1977), *trans*-$[PtI_2(PCy_3)_2]$ 2.622 (1) Å (Alcock & Leviston, 1974), where Cy is cyclohexyl, and *trans*-$[PtI_2(PC_{18}F_{15})_2]$ 2.626 (2) Å (Hunter, Muir & Sharp, 1986). One would expect longer coordinated halide bonds in platinum–phosphine complexes than in the corresponding platinum–arsine compounds.

Experimental

The title compound was isolated as a substitution product from the reaction between *trans*-chloromethylbis(triphenylarsine)platinum(II) and I^-. Repeated recrystallization from chloroform yielded bright orange cubes of the title compound. The explanation for the formation of this unexpected substitution product lies in the sequential oxidative addition of trace amounts of HCl impurity in the chloroform to the substitution product *trans*-$[PtI(CH_3)(AsPh_3)_2]$ to form *trans*-$[PtClI(H)(CH_3)(AsPh_3)_2]$. This compound then undergoes a reductive elimination step where the hydrogen and methyl groups are eliminated as methane, followed by substitution of the chloride by the excess I^- present in solution to form the final Pt^{II} species.

Crystal data

$[PtI_2(C_{18}H_{15}As)_2]$
$M_r = 1061.37$
Triclinic
$P\bar{1}$
$a = 10.433 (4)$ Å
$b = 12.538 (5)$ Å
$c = 13.270 (5)$ Å
$\alpha = 84.71 (3)°$
$\beta = 77.78 (3)°$
$\gamma = 78.42 (3)°$
$V = 1659.7 (1.1)$ Å^3
$Z = 2$
$D_x = 2.124$ Mg m^{-3}
$D_m = 2.096$ Mg m^{-3}
D_m measured by flotation in tallous carbonate/formic acid (85%)

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 15–21°$
$\mu = 8.09$ mm^{-1}
$T = 293 (2)$ K
Cube
0.26 × 0.24 × 0.20 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical (Akselrud, Grin, Zavalii, Pecharsky & Fundamuntsky, 1989)
$T_{min} = 0.109$, $T_{max} = 0.198$
3072 measured reflections
3072 independent reflections

2900 reflections with $I > 3\sigma(I)$
$\theta_{max} = 22.5°$
$h = 0 \rightarrow 8$
$k = -12 \rightarrow 13$
$l = -13 \rightarrow 14$
3 standard reflections every 100 reflections intensity decay: <1%

Refinement

Refinement on F^2
$R(F) = 0.0397$
$wR(F^2) = 0.1143$
$S = 1.085$
2900 reflections
374 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0772P)^2 + 20.731P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.081$
$\Delta\rho_{max} = 2.179$ e Å^{-3}
$\Delta\rho_{min} = -1.625$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Pt1—As1	2.405 (2)	Pt2—As2	2.402 (2)
Pt1—I1	2.630 (2)	Pt2—I2	2.6312 (14)
As1—C131	1.941 (13)	As2—C231	1.945 (13)
As1—C111	1.952 (14)	As2—C211	1.953 (15)
As1—C121	1.955 (14)	As2—C221	1.97 (2)
As1^{i}—Pt1—I1	91.93 (6)	As2—Pt2—I2	87.49 (5)
As1—Pt1—I1	88.07 (6)	As2^{ii}—Pt2—I2	92.51 (5)
C131—As1—C111	104.3 (6)	C231—As2—C211	103.1 (6)
C131—As1—C121	100.1 (6)	C231—As2—C221	101.2 (6)
C111—As1—C121	101.8 (6)	C211—As2—C221	103.5 (7)
C131—As1—Pt1	115.9 (4)	C231—As2—Pt2	115.0 (4)
C111—As1—Pt1	114.1 (4)	C211—As2—Pt2	115.8 (4)
C121—As1—Pt1	118.4 (4)	C221—As2—Pt2	116.2 (4)
I1—Pt1—As1—C131	−46.5 (5)	I2—Pt2—As2—C231	49.2 (5)
I1—Pt1—As1—C111	74.7 (5)	I2—Pt2—As2—C211	−71.0 (5)
I1^{i}—Pt1—As1—C121	14.6 (5)	I2—Pt2—As2—C221	167.2 (5)

Symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $-x, -y, 1 - z$.

Table 2. *Displacement of atoms (Å) and angles (°) of the phenyl planes from the square-coordination plane defined by the As and I atoms*

Atom	Distance	Atom	Distance
C111	−1.72 (1)	C211	−1.66 (1)
C114	−4.13 (2)	C214	−4.01 (2)
C121	0.43 (2)	C221	0.39 (2)
C124	1.17 (2)	C224	1.10 (3)
C131	1.27 (1)	C231	1.33 (1)
C134	3.24 (2)	C234	3.35 (2)

Ring	Molecule 1	Molecule 2
Phenyl 1	65.7 (3)	61.5 (3)
Phenyl 2	79.0 (4)	88.3 (4)
Phenyl 3	66.1 (4)	73.2 (4)

Data was only collected to $\theta = 22.5°$ due to substantial peak broadening at larger θ values. This also resulted in a rather low ratio of refined reflections to parameters. Four high residual electron-density peaks of *ca* 1–2 e Å^{-3} within 1.5 Å of the Pt and I atoms were attributed to insufficient absorption correction due to the abundance of high electron-scattering atoms in the structure.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *PROFIT* (Streltsov & Zavodnik, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AB1414). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(6-chloro-2-pyridonato-*N*,*O*)(4,4′-dimethyl-2,2′-bipyridine-*N*,*N*′)zinc(II) Hydrate at 150 K

Christopher G. Mowat, Simon Parsons, Gregory A. Solan and Richard E. P. Winpenny

Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland. E-mail: s.parsons@ed.ac.uk

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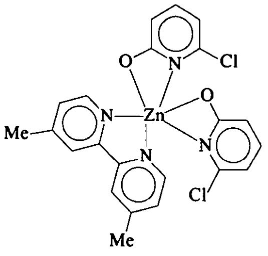
Abstract

The title compound, bis(6-chloro-2-pyridinolato-*N*,*O*)-(4,4′-dimethyl-2,2′-bipyridine-*N*,*N*′)zinc(II) hydrate, [$Zn(C_5H_3ClNO)_2(C_{12}H_{12}N_2)$].$H_2O$, is an example of a pyridonate complex of zinc. The complex has a distorted geometry imposed by the narrow bite angles of the ligands.

Comment

The pyridonate ligand has been widely used in the coordination chemistry of second and third row transition metals, but to a lesser degree with the first row metals. Our interest in this ligand with the 3*d* metals Mn, Fe, Co, Ni and Cu has resulted in a number of unusual structural types (see, for example, Brechin, Harris, Parsons & Winpenny, 1996; Parsons, Solan & Winpenny, 1995). In this paper, we report the preparation and crystal structure of [$Zn(chp)_2(Me_2\text{-}bipy)$].$H_2O$, (1).$H_2O$ (chp is 6-chloro-2-pyridonate and bipy is 2,2′-bipyridine), which was obtained as part of the extension of our results involving zinc.



(1)

Compound (1) is an example of a pyridone complex of zinc (Fig. 1). While the Zn—N bond lengths to the N atoms (N1 and N1′) of the bipyridine ligand adopt normal values and are not significantly different, chemically similar bonds to the pyridonate ligands do differ, by 0.058 (4) Å in the case of Zn—O1*R* and Zn—O2*R*, and by 0.136 (4) Å in the case of Zn—N1*R* and Zn—N2*R*. The coordination geometry of complex (1) is irregular because of the characteristically narrow bite angles of the ligands, but can be very roughly described as 'distorted octahedral'. The longer Zn—O bond [Zn—O1*R* 2.097 (3) Å] lies *trans* with respect to Zn—N1 [2.098 (3) Å], while the shorter bond [Zn—O2*R* 2.039 (3) Å] is *trans* to Zn—N1*R* [2.237 (3) Å]. This is

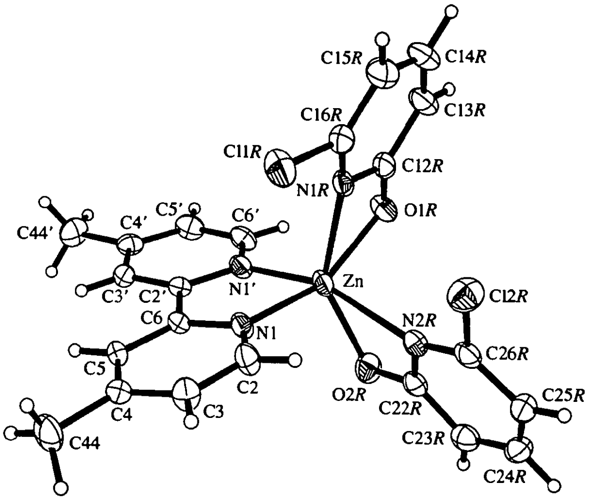


Fig. 1. A view of the title complex with the atom-numbering scheme. Displacement ellipsoids enclose 50% probability surfaces.