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Three Pt^{II} catecholate and 1,2-dithiocatecholate complexes

M. J. Gerald Lesley,[a]† William Clegg,[b] Todd B. Marder,[c]† Nicholas C. Norman,[a] A. Guy Orpen,[a] Andrew J. Scott[b] and Jonathan Starbuck[a]

[a]*School of Chemistry, University of Bristol, Cantocks Close, Bristol BS8 1TS, England,* [b]*Department of Chemistry, University of Newcastle, Newcastle upon Tyne NE1 7RU, England, and* [c]*Department of Chemistry, University of Durham, Science Laboratories, South Road, Durham DH1 3LE, England. E-mail: n.c.norman@bris.ac.uk*

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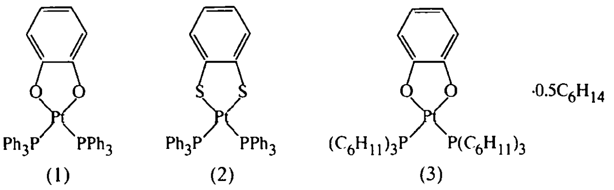
Abstract

In the crystal structures of the three title complexes, (benzene-1,2-diolato-*O*,*O*′)bis(triphenylphosphine)platinum(II), [$Pt(C_6H_4O_2)(C_{18}H_{15}P)_2$], (1), (benzene-1,2-dithiolato-*S*,*S*′)bis(triphenylphosphine)platinum(II), [$Pt(C_6H_4S_2)(C_{18}H_{15}P)_2$], (2), and the *n*-hexane hemisolvate of (benzene-1,2-diolato-*O*,*O*′)bis(tricyclohexylphosphine)platinum(II), [$Pt(C_6H_4O_2)(C_{18}H_{33}P)_2]\cdot0.5C_6H_{14}$, (3), the Pt atoms are tetracoordinate with distorted square-planar geometry. Compounds (1) and (2) are isostructural.

Comment

Metal catecholates have been extensively studied due to their unique electronic (Bhattacharya & Pierpont, 1992), magnetic (Coucouvanis *et al.*, 1993) and catalytic activity (Persson & Andersson, 1993). Metal thiolates are important as biological electron-transfer mediators (Blower & Dilworth, 1987). While many catecholate and thiocatecholate complexes have been characterized, for platinum, there are only two closely related cases where the crystal structures are known, namely [Pt{1,2-O_2-3,5-$(NO_2)_2C_6H_2$}$(PMe_2Ph)_2$] (Clemente *et al.*, 1994) and [Pt{1,2-O_2-4,5-(3-ethynylthiophene)$_2C_6H_2$}$(PPh_3)_2$] (Kinder & Youngs, 1996). Other related compounds containing group ten elements and catecholate or thiocatecholate derivatives have also been structurally characterized (Abakumov *et al.*, 1996; Pierpont & Downs, 1975; Darkwa, 1997; Cao *et al.*, 1996).

Selected bond lengths and angles are given for complexes (1), (2) and (3) in Tables 1, 2 and 3, respectively. The Pt—P bond lengths for (2) [mean Pt—P bond length of 2.283 (7) Å] compared with (1) [mean Pt—P 2.247 (6) Å] are consistent with the thiocatecholate group having a stronger *trans* influence than the catecholate group. The increased steric bulk of the $P(C_6H_{11})_3$ ligand compared with PPh_3 [cone angles of 170 and 145°, respectively (Tolman, 1977)] leads to a larger P—Pt—P angle (by approximately 11°) for (3) than for (1) and (2). This results in smaller O—Pt—P angles for (3) [mean 85.0 (5)°] compared with the mean O—Pt—P angle for (1) [91 (5)°] and the mean S—Pt—P angle for (2) [89 (3)°]. The bite angles of the chelating ligands are consistent with the larger radius of sulfur compared with oxygen.



Significantly more distortion of the atoms that define the square plane around platinum is observed for (2) than for (1) or (3). The average displacement of the atoms from the square plane defined by Pt, P and S in (2) is 0.20 (4) Å [maximum of 0.250 (1) Å for S1] compared with mean values of 0.10 (2) Å for (1) and 0.058 (12) Å

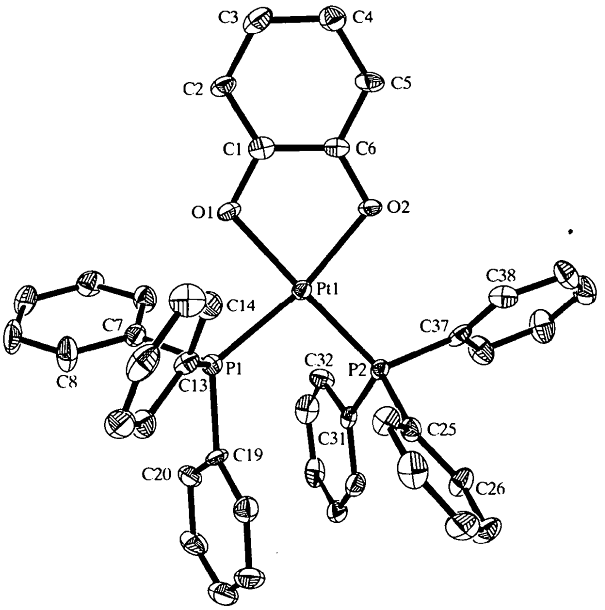


Fig. 1. The structure of (1) with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity.

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† MJGL and TBM also carried out this work at the Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1.

for (3), where Pt, P and O define the square plane. A larger twist between the C_6 ring of the chelating ligand and the platinum square plane is also observed for (2) [15.2 (2)°] than for (1) [9.8 (3)°] and (3) [7.8 (3)°].

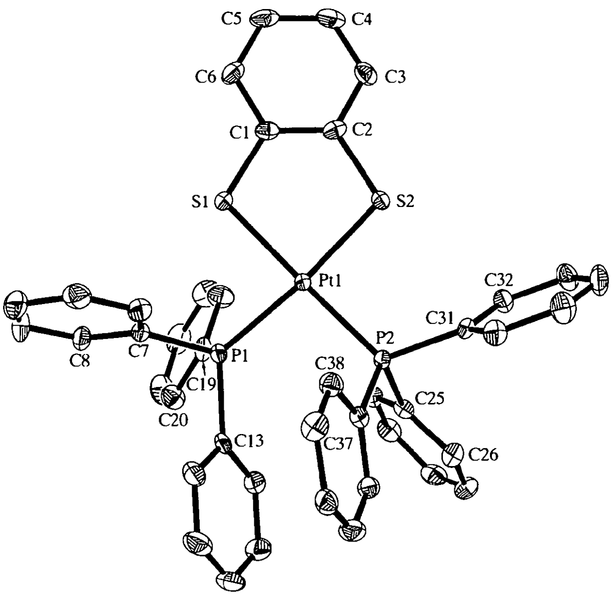

Fig. 2. The structure of (2) with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity.

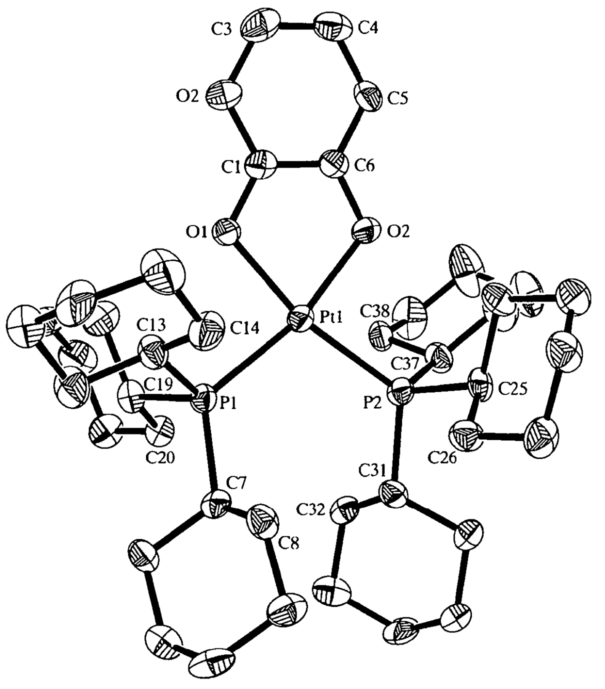

Fig. 3. The structure of (3) with displacement ellipsoids drawn at the 50% probability level. H atoms and the hexane solvent molecule have been omitted for clarity.

Refinement of the Flack (1983) parameter for (1) indicated substantial twinning.

Experimental

Compounds (1) and (3) were formed as minor products from phosphine-exchange reactions between *cis*-$[Pt(PPh_3)_2(Bcat)_2]$ (cat = 1,2-$O_2C_6H_4$) and bis(dicyclohexylphosphino)ethane (dcpe) or $P(C_6H_{11})_3$, respectively (Curtis *et al.*, 1999). Compound (2) was formed in the attempted catalysed diboration of an internal alkyne with the diborane (4) compound, B_2(thiocat)$_2$ (thiocat = 1,2-$S_2C_6H_4$) (Lesley *et al.*, 1996). Compounds (1)–(3) are believed to be by-products formed from exposure to trace amounts of oxygen or water. Compound (1) was crystallized from a CD_2Cl_2/hexane mixture, (2) from a $CDCl_3$/hexane mixture and (3) from a toluene/hexane mixture.

Compound (1)

Crystal data

$[Pt(C_6H_4O_2)(C_{18}H_{15}P)_2]$
$M_r = 827.72$
Monoclinic
Pn
$a = 9.0064 (14)$ Å
$b = 10.8717 (11)$ Å
$c = 17.585 (2)$ Å
$\beta = 103.717 (11)°$
$V = 1672.7 (4)$ Å^3
$Z = 2$
$D_x = 1.643$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 223 reflections
$\theta = 1.87–27.49°$
$\mu = 4.327$ mm^{-1}
$T = 173 (2)$ K
Block
0.3 × 0.2 × 0.2 mm
Orange

Data collection

Siemens SMART CCD diffractometer
ω rotation with narrow frames
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{min} = 0.252$, $T_{max} = 0.421$
10 596 measured reflections
3843 independent reflections (plus 1428 Friedel-related reflections)

4680 reflections with $I > 2\sigma(I)$
$R_{int} = 0.046$
$\theta_{max} = 27.49°$
$h = -11 \rightarrow 7$
$k = -14 \rightarrow 14$
$l = -20 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.081$
$S = 0.970$
5271 reflections
425 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0370P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 2.928$ e Å^{-3}
$\Delta\rho_{min} = -1.982$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.44 (1)

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

Pt1—O2	2.042 (6)	Pt1—P2	2.241 (2)
Pt1—O1	2.056 (6)	Pt1—P1	2.252 (3)

O2—Pt1—O1	82.8 (2)	O2—Pt1—P1	166.0 (2)
O2—Pt1—P2	95.3 (2)	O1—Pt1—P1	85.7 (2)
O1—Pt1—P2	174.4 (2)	P2—Pt1—P1	96.86 (8)

Compound (2)

Crystal data

$[Pt(C_6H_4S_2)(C_{18}H_{15}P)_2]$
$M_r = 859.84$
Monoclinic
Pn
$a = 9.0177\ (7)$ Å
$b = 10.9977\ (8)$ Å
$c = 17.9351\ (12)$ Å
$\beta = 102.093\ (2)°$
$V = 1739.2\ (2)$ Å^3
$Z = 2$
$D_x = 1.642$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 9848 reflections
$\theta = 1.85–28.43°$
$\mu = 4.276$ mm^{-1}
$T = 160\ (2)$ K
Block
$0.16 \times 0.12 \times 0.10$ mm
Orange

Data collection

Siemens SMART CCD diffractometer
ω rotation with narrow frames
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{min} = 0.552$, $T_{max} = 0.655$
10 615 measured reflections
4384 independent reflections (plus 927 Friedel-related reflections)

5236 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 28.44°$
$h = -12 \rightarrow 8$
$k = -13 \rightarrow 13$
$l = -23 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.047$
$S = 1.124$
5311 reflections
424 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0215P)^2 + 2.1895P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.537$ e Å^{-3}
$\Delta\rho_{min} = -0.895$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = $-0.006\ (4)$

Table 2. *Selected geometric parameters (Å, °) for (2)*

Pt1—P2	2.2730 (10)	Pt1—S2	2.3070 (10)
Pt1—P1	2.2930 (11)	Pt1—S1	2.3082 (10)
P2—Pt1—P1	97.23 (4)	P2—Pt1—S1	169.08 (4)
P2—Pt1—S2	91.22 (4)	P1—Pt1—S1	86.04 (4)
P1—Pt1—S2	164.68 (4)	S2—Pt1—S1	88.04 (4)

Compound (3)

Crystal data

$[Pt(C_6H_4O_2)(C_{18}H_{33}P)_2]\cdot0.5C_6H_{14}$
$M_r = 907.10$
Monoclinic
$P2_1/n$
$a = 10.338\ (2)$ Å
$b = 16.142\ (3)$ Å
$c = 26.162\ (4)$ Å
$\beta = 93.952\ (10)°$
$V = 4355.7\ (12)$ Å^3
$Z = 4$
$D_x = 1.383$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 178 reflections
$\theta = 1.48–24.75°$
$\mu = 3.329$ mm^{-1}
$T = 173\ (2)$ K
Needle
$0.4 \times 0.1 \times 0.1$ mm
Orange

Data collection

Siemens SMART CCD diffractometer
ω rotation with narrow frames
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{min} = 0.571$, $T_{max} = 0.717$

22 033 measured reflections
7428 independent reflections
4705 reflections with $I > 2\sigma(I)$
$R_{int} = 0.102$
$\theta_{max} = 24.75°$
$h = -12 \rightarrow 9$
$k = -18 \rightarrow 19$
$l = -30 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.092$
$S = 1.029$
7398 reflections
452 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0221P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.026$

$\Delta\rho_{max} = 0.919$ e Å^{-3}
$\Delta\rho_{min} = -0.688$ e Å^{-3}
Extinction correction: *SHELXTL* (Siemens, 1995*a*)
Extinction coefficient: 0.00031 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (3)*

Pt1—O2	2.033 (5)	Pt1—P1	2.265 (2)
Pt1—O1	2.051 (5)	Pt1—P2	2.268 (2)
O2—Pt1—O1	82.3 (2)	O2—Pt1—P2	85.5 (2)
O2—Pt1—P1	166.33 (15)	O1—Pt1—P2	166.8 (2)
O1—Pt1—P1	84.45 (15)	P1—Pt1—P2	107.96 (8)

H atoms were constrained to idealized geometries with a riding model and were assigned isotropic displacement parameters $U(H) = 1.2U_{iso}(C)$. The large residual electron-density peaks for (1) (~1 Å from Pt) may be associated with relatively poor crystal quality. The large value for R_{int} for (3) (> 0.1) is likely to be due to the relatively low intensity of the diffraction data, coupled with moderately high absorption.

For all compounds, data collection: *SMART* (Siemens, 1995*b*). Cell refinement: *SAINT* (Siemens, 1995*b*) for (1) and (3); local programs for (2). For all compounds, data reduction: *SAINT*; program(s) used to solve structures: *SHELXTL* (Siemens, 1995*a*); program(s) used to refine structures: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1077). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1275–1278

Tetrachlorotetrakis(propan-2-ol)uranium(IV) and tetrachlorotetrakis(propan-2-ol)thorium(IV)

Pamela L. Gordon,[a] Julia A. Thompson,[b] John G. Watkin,[c] Carol J. Burns,[c] Nancy N. Sauer[c] and Brian L. Scott[c]

[a]*Callaway Golfball Company, 2285 Rutherford Road, Carlsbad, CA 92008-8815, USA,* [b]*PolyIonix Separation Technologies Inc., Dayton, NJ 08810, USA, and* [c]*Los Alamos National Laboratory, Los Alamos, NM 87545, USA. E-mail: nsauer@lanl.gov*

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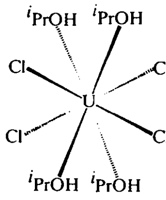
Abstract

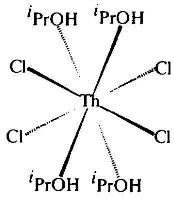
The title complexes, [$UCl_4(C_3H_8O)_4$] and [$ThCl_4(C_3H_8O)_4$], are isomorphous and crystallize in the tetragonal space group $I4_1/a$. The molecules have approximate dodecahedral symmetry and occupy sites of $\bar{4}$ symmetry. Principal bond lengths include U—Cl = 2.6478 (10), U—O = 2.478 (3), Th—Cl = 2.7066 (8) and Th—O = 2.515 (2) Å.

Comment

In previous publications, we have examined the direct reaction between lanthanide and actinide metals and elemental iodine, employing either tetrahydrofuran (THF) or alcohols as solvent (Barnhart *et al.*, 1995; Van der Sluys *et al.*, 1992). We have now extended these studies to include the reaction of thorium and uranium metal turnings with chlorine gas, which may be conveniently bubbled through a flask containing isopropanol solvent and the appropriate actinide metal. Subsequent work-up provides crystals of uranium or thorium tetrachloride which contain four coordinated molecules of isopropanol. $UCl_4(^i PrOH)_4$ (Smith *et al.*, 1969) and $ThCl_4(^i PrOH)_4$ (El Aggan, 1973) have been described previously but they have not been structurally characterized. We report here the structural characterization of tetrachlorotetrakis(isopropanol)uranium(IV), (I), and tetrachlorotetrakis(isopropanol)thorium(IV), (II).



(I)



(II)

Complexes (I) and (II) are isostructural and crystallize in the tetragonal space group $I4_1/a$. The complexes occupy sites of $\bar{4}$ symmetry (Figs. 1 and 2). The ligands define a somewhat distorted dodecahedral structure about the metal center, with the chloride ligands occupying '*B*' sites and the isopropanol ligands occupying '*A*' sites (Kepert, 1978).

The U—Cl distance of 2.6478 (10) Å is slightly longer than the mean value of 2.595 (2) Å observed in seven-coordinate $UCl_4(thf)_3$ (Van der Sluys *et al.*, 1993),

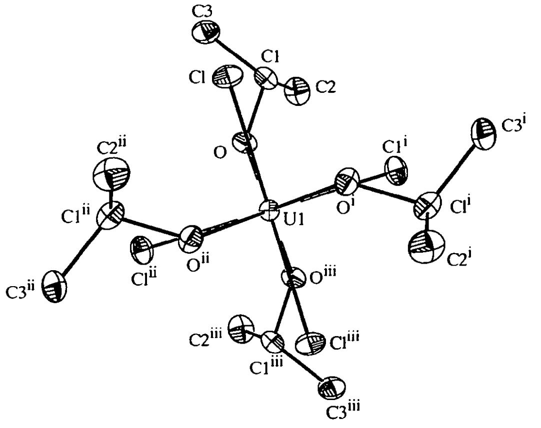


Fig. 1. The molecular structure of (I), showing the atom-numbering scheme and with 50% probability displacement ellipsoids. H atoms have been omitted for clarity. The view is down the fourfold axis of the $\bar{4}$ symmetry element [symmetry codes: (i) $y - \frac{1}{4}, \frac{5}{4} - x, \frac{1}{4} - z$; (ii) $\frac{5}{4} - y, \frac{1}{4} + x, \frac{1}{4} - z$; (iii) $1 - x, \frac{3}{2} - y, z$].

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