# [(1,2:5,6-η)-Cycloocta-1,5-diene]bis[2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene-thiolato]platinum(II)

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The title complex, [Pt(C$_7$F$_7$S)$_2$(C$_8$H$_{12}$)], has twofold rotation symmetry, with the Pt^{II} ion in an approximately square-planar coordination geometry.

Comment

We have a long-standing interest in transition metal complexes bearing fluorinated thiolates (Arroyo *et al.*, 2000; Villanueva *et al.*, 2004; Jones *et al.*, 2005), since these compounds are relevant to the study of fluorous biphasic catalytic processes (Barthel-Rosa & Gladysz, 1999) and are often involved in chemical systems promoting C—F bond activation (Murai, 1999; Torrens, 2005). As part of a project to develop metalloligand-type compounds, we have found that the metathetical reactions of [PtCl$_2$(η^2,η^2-COD)], where COD is cycloocta-1,5-diene, with a variety of lead fluorothiolates Pb(S*Rf*)$_2$ (*Rf* = C$_6$F$_5$, C$_6$HF$_4$-4, CH$_2$C$_6$H$_4$F-2 and CH$_2$CF$_3$) afford the expected Pt^{II} complexes. Such a reaction was used for the synthesis of the title complex, (I).

(I)
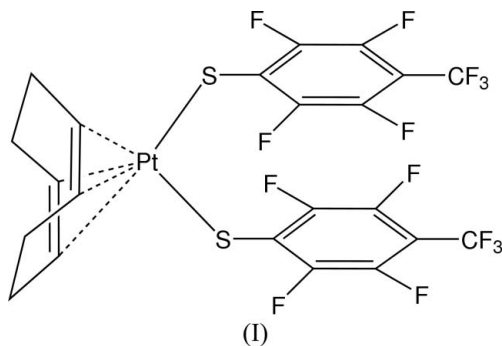
A single-crystal X-ray structure analysis of (I) shows that the metal centre lies on a twofold axis (Fig. 1). Considering the mid-points of the C8≡C11^i and C11≡C8^i double bonds as coordination sites [symmetry code: (i) $1 - x$, y, $\frac{3}{2} - z$], the coordination around the Pt^{II} ion approximates a square-planar geometry. The Pt—S bond length (Table 1) is in good agreement with those previously observed for the same thiolate coordinated in a terminal [2.306 (4) and 2.325 (4) Å] or μ_2-bridging mode [2.323 (3) and 2.326 (3) Å] (Rivera *et al.*, 2001). For the closely related complex *trans*-[Pt(SC$_6$F$_5$)$_2$(SEt$_2$)$_2$] the Pt—S$_{thiolate}$ bond length is 2.323 (1) Å (Cruz-Garritz *et al.*, 1990). Variations for Pt—S$_{thiolate}$ bonds in this class of compounds seem then to be limited to a small range. The S atoms in (I) have a tetrahedral geometry, as expected for an sp^3 hybridization state. The COD ligand is coordinated, as usual, in an η^2,η^2 manner and adopts a tub conformation (D_{2d} local symmetry).

The exact C_2 symmetry adopted by (I) and the lack of mirror symmetry allows *cis*-benzene rings to be displaced in order to avoid steric hindrance between CF$_3$ groups. As a consequence, although the benzene planes are almost parallel, no π–π interactions are present. The packing involves no significant intermolecular interactions.

Experimental

To a solution of [PtCl$_2$(η^2,η^2-COD)] (150 mg, 0.4 mmol) in acetone (25 ml) was added a solution of Pb(SC$_6$F$_4$CF$_3$-4)$_2$ (283 mg, 0.4 mmol) in acetone (25 ml). The reaction mixture rapidly turned yellow. The white precipitate formed (PbCl$_2$) was filtered off and the yellow solution evaporated under vacuum to give (I) as a yellow microcrystalline solid (yield 292 mg, 92%). Single crystals of (I) were obtained by slow evaporation of an acetone solution under a stream of N$_2$.

Crystal data

[Pt(C$_7$F$_7$S)$_2$(C$_8$H$_{12}$)]
$M_r = 801.53$
Monoclinic, $C2/c$
$a = 18.4374\,(15)$ Å
$b = 12.9716\,(10)$ Å
$c = 13.3604\,(11)$ Å
$\beta = 131.392\,(3)°$
$V = 2397.1\,(3)$ Å^3

$Z = 4$
$D_x = 2.221$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 6.15$ mm^{-1}
$T = 298\,(1)$ K
Irregular fragment, yellow
$0.38 \times 0.28 \times 0.20$ mm

Data collection

Bruker $P4$ diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scan
($XSCANS$; Siemens, 1996)
$T_{min} = 0.180$, $T_{max} = 0.290$
4611 measured reflections
3499 independent reflections

2908 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 30.0°$
3 standard reflections
  every 97 reflections
  intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.071$
$S = 1.03$
3499 reflections
205 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0237P)^2 + 4.9564P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.78$ e Å^{-3}
$\Delta\rho_{min} = -0.83$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pt1—S1	2.3245 (11)	Pt1—C11	2.188 (4)
Pt1—C8	2.200 (5)	C8—C11^i	1.376 (8)
C11—Pt1—C8	81.1 (2)	C11—Pt1—S1	87.63 (15)
C11—Pt1—C11^i	93.3 (3)	C11—Pt1—S1^i	163.48 (17)
C8^i—Pt1—C8	91.4 (3)	S1^i—Pt1—S1	96.15 (5)
C8—Pt1—S1	158.78 (16)	C1—S1—Pt1	108.63 (13)
C8^i—Pt1—S1	90.04 (15)		

Symmetry code: (i) $-x+1, y, -z+\frac{3}{2}$.

The trifluoromethyl group is highly disordered and was modelled using two positions for each F atom, one set of three F atoms being rotated by *ca* 60° with respect to the other. Site-occupation factors for
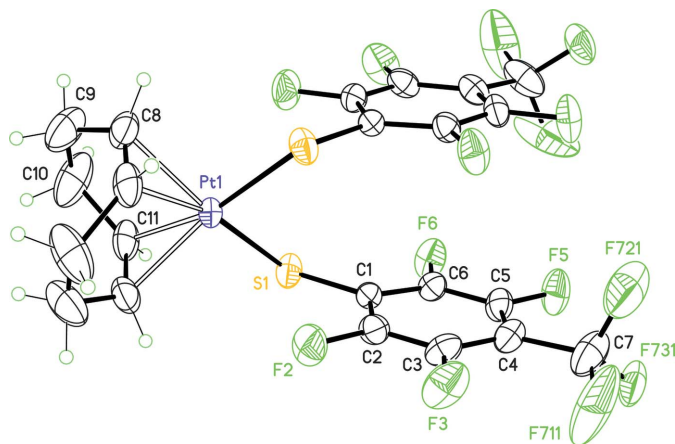

Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 30% probability level. Unlabelled atoms are related by the symmetry code $(1 - x, y, \frac{3}{2} - z)$. The minor component of the disordered CF$_3$ group has been omitted for clarity.

each component refined to 0.671 (16) for F711/F721/F731 and 0.329 (16) for F712/F722/F732. The geometry for each group was restrained in order to maintain a sensible geometry: C—F = 1.31 (1) Å and F⋯F = 2.09 (2) Å. The F atoms were restrained to approximate isotropic behaviour. H atoms for the COD ligand were positioned geometrically and refined using a riding model, with bond lengths constrained to 0.97 (methylene CH$_2$) or 0.98 Å (Csp^2—H), and with U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

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