

Tetrakis(2,3,5,6-tetrafluorobenzenethiolato- κS)-(triphenylphosphine- κP)osmium(IV) *n*-hexane hemisolvateMargarita Cerón,^a Maribel Arroyo^a and Sylvain Bernès^{b*}^aCentro de Química del Instituto de Ciencias, BUAP, Puebla, Pue., Mexico, and ^bDEP Facultad de Ciencias Químicas, UANL, Guerrero y Progreso S/N, Col. Treviño, 64570 Monterrey, NL, MexicoCorrespondence e-mail:
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Key indicators

Single-crystal X-ray study
 $T = 296$ K
Mean $\sigma(C-C) = 0.015$ Å
Disorder in solvent or counterion
 R factor = 0.064
 wR factor = 0.174
Data-to-parameter ratio = 13.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

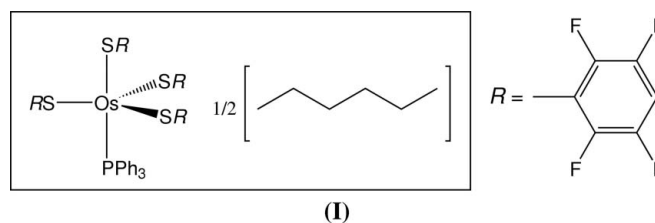
The title compound, $[\text{Os}(\text{C}_6\text{HF}_4\text{S})_4(\text{PPh}_3)] \cdot 0.5\text{C}_6\text{H}_{14}$, includes a trigonal-bipyramidal Os^{IV} complex with a coordination geometry close to that known for the analogous unsolvated complex, and hexane disordered around an inversion centre. Significant libration and rotation are observed for the thiolate ligands in the crystal structure when compared with the unsolvated species.

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Comment

Five-coordinate Os complexes are rather uncommon, representing fewer than 10% of the X-ray characterized mononuclear Os complexes in the Cambridge Structural Database (CSD, Version 5.27, updated May 2006; Allen, 2002). We have for a long time been involved in the synthesis and study of the reactivity of five-coordinate Os^{IV} complexes of general formula $[\text{Os}(\text{thiolate})_4(\text{phosphine})]$. Using a variety of fluorinated thiolate and substituted phosphine ligands, we have found that these complexes are based on a trigonal-bipyramidal coordination geometry. One structurally characterized complex belonging to this research is $[\text{Os}(\text{SC}_6\text{F}_4\text{H})_4(\text{PPh}_3)]$, where the thiolate ligand is 2,3,5,6-tetrafluorobenzenethiolate (Arroyo *et al.*, 1994). During the preparation of a batch of this complex for thermolysis studies, we obtained the title hexane hemisolvate complex, (I), and report its structure here.



The trigonal-bipyramidal Os^{IV} complex, (I) (Fig. 1, Table 1), reveals a coordination geometry close to that previously observed for the unsolvated complex (Arroyo *et al.*, 1994). Hexane molecules are disordered around an inversion centre. Crystals of (I) slowly lose solvent during data collection (see *Experimental*), while the unsolvated complex is stable under X-ray irradiation. The solvent inclusion does not affect the crystal symmetry: both compounds crystallize in the space group $P\bar{1}$ with similar unit-cell parameters. However, the molecular geometry of the Os^{IV} complex is significantly affected by solvent inclusion, mainly regarding the thiolate ligands (Fig. 2). The $\text{C}_6\text{F}_4\text{H}$ substituents of the equatorial ligands are allowed to librate in planes approximately normal to their $\text{Os}-\text{S}_{\text{eq}}$ bonds, and the amplitude of these oscillations ranges from *ca* 18.9° ($\text{S}2$ -ligand) to 36.8° ($\text{S}3$ -ligand). The axial

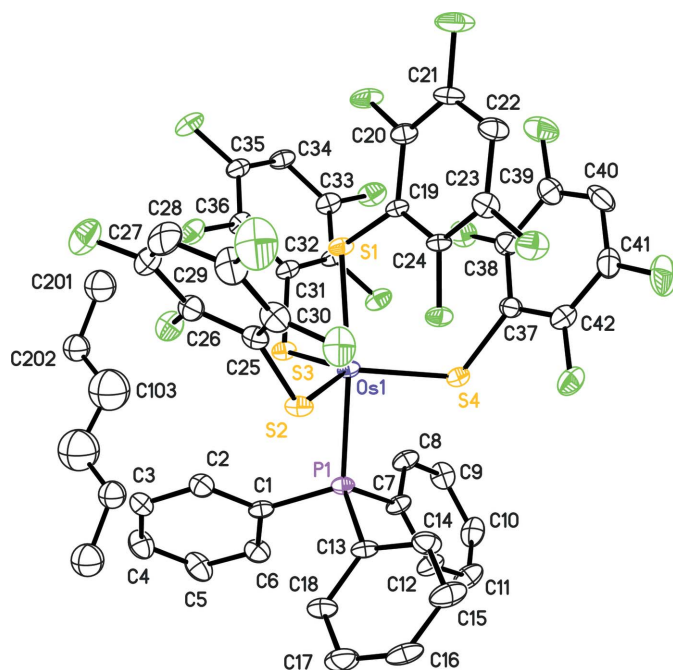


Figure 1
The structure of (I), with displacement ellipsoids drawn at the 15% probability level and the atom-labelling scheme for the asymmetric unit. Only one of the two orientations of hexane is shown. Unlabelled atoms are related to labelled atoms by the symmetry operator $(2 - x, -y, 1 - z)$. H atoms have been omitted for clarity.

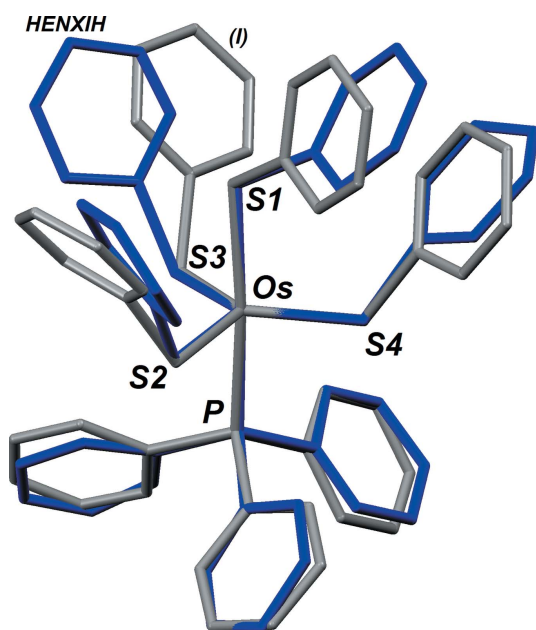


Figure 2
A least-squares overlay of complex (I) and the corresponding unsolvated complex (Arroyo *et al.*, 1994; CSD refcode HENXIH). For the sake of clarity, H and F atoms have been omitted. The fit has been carried out on Os, S and P atoms using the overlay facility of *MERCURY* (version 1.4.1; Macrae *et al.*, 2006). The calculated r.m.s. deviation for the fit of these atoms is 0.062 Å. The labelling scheme corresponds to that used for (I).

ligand S1 is affected by non-restricted rotations about the Os—S1 and S1—C19 σ bonds (*ca* 23.7 and 29.1°, respectively). Such motions have previously been observed in the closely

related complex $[\text{Os}(\text{SC}_6\text{F}_5)_4(\text{PPh}_3)]$, which crystallizes with three molecules in the asymmetric unit (Mendoza *et al.*, 2006).

It thus seems that complexes of the form $[\text{Os}(\text{thiolate})_4(\text{phosphine})]$ adopt a rigid arrangement for the $[\text{OsS}_4\text{P}]$ coordination core, while the substituents of the thiolate ligands are rather flexible in both solvated and unsolvated species.

Experimental

The title compound was prepared by reacting 2,3,5,6-tetrafluorobenzenethiol (0.80 ml, 6 mmol), OsO_4 (0.25 g, 1 mmol) and PPh_3 (1.60 g, 6 mmol) in refluxing ethanol (25 ml), for 3.5 h. During that time, a dark-green precipitate appeared. The mixture was cooled to 298 K and kept at that temperature without stirring for 16 h. The precipitate, identified as $[\text{Os}(\text{SC}_6\text{F}_4\text{H})_4(\text{PPh}_3)]$, was isolated by filtration (92% yield). From the filtrate, the solvent was distilled off under reduced pressure. The resulting solid was chromatographed on silica gel, using a solvent mixture of hexane— CH_2Cl_2 (4:1) as eluent, affording (I). Single crystals of (I) were produced by slow evaporation of the eluent (0.15% yield).

Crystal data

$[\text{Os}(\text{C}_6\text{HF}_4\text{S})_4(\text{C}_{18}\text{H}_{15}\text{P})] \cdot 0.5\text{C}_6\text{H}_{14}$
 $M_r = 1220.07$
 Triclinic, $P\bar{1}$
 $a = 12.209$ (3) Å
 $b = 13.513$ (3) Å
 $c = 13.865$ (3) Å
 $\alpha = 89.20$ (2)°
 $\beta = 87.40$ (2)°
 $\gamma = 86.454$ (15)°

$V = 2280.5$ (9) Å³
 $Z = 2$
 $D_x = 1.777$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 3.11$ mm⁻¹
 $T = 296$ (1) K
 Plate, dark red
 $0.60 \times 0.22 \times 0.08$ mm

Data collection

Bruker *P4* diffractometer
 ω scans
 Absorption correction: ψ scan
 (*XSCANS*; Siemens, 1996)
 $T_{\min} = 0.566$, $T_{\max} = 0.778$
 8756 measured reflections
 8033 independent reflections

6378 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.042$
 $\theta_{\max} = 25.0^\circ$
 3 standard reflections
 every 97 reflections
 intensity decay: 28.1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.065$
 $wR(F^2) = 0.174$
 $S = 1.05$
 8033 reflections
 597 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1011P)^2 + 7.7358P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 2.48$ e Å⁻³
 $\Delta\rho_{\min} = -2.06$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Os1—S4	2.204 (3)	Os1—P1	2.396 (3)
Os1—S2	2.218 (3)	Os1—S1	2.420 (2)
Os1—S3	2.219 (2)		
S4—Os1—S2	124.39 (11)	S3—Os1—P1	84.86 (9)
S4—Os1—S3	114.73 (10)	S4—Os1—S1	99.87 (10)
S2—Os1—S3	118.87 (11)	S2—Os1—S1	95.23 (10)
S4—Os1—P1	85.47 (10)	S3—Os1—S1	88.55 (9)
S2—Os1—P1	85.53 (9)	P1—Os1—S1	172.84 (9)

Although it is an air-stable complex, (I) is damaged by X-ray irradiation, probably because of gradual solvent release. This behaviour is confirmed by the fact that a two-year old sample of (I) still exhibited IR bands characteristic of hexane. The hexane molecule is disordered over two sites related by an inversion centre. Atom C103, with a site occupation factor (s.o.f.) of 1, is close to the inversion centre, forming the central C—C bond of the hexane molecule, while atoms C101 and C102 are disordered with C201 and C202, each with an s.o.f. of 0.5. Attempts to refine the s.o.f. did not converge to a more satisfactory model. This solvent molecule was refined isotropically and its geometry was regularized using suitable restraints: all C—C σ bonds were restrained to 1.54 (1) Å, and 1,3 distances along the C—C normal chain were restrained to 2.49 (2) Å. In order to obtain a sensible geometry for the PPh₃ and thiolate ligands, the C atoms of each ring were restrained to lie in a common plane (chiral volumes defined by tetrahedra restrained to zero with an s.u. of 0.05 Å³) and twofold symmetry was applied to the six-membered rings, within an s.u. of 0.02 Å. Similarity restraints were applied, with an s.u. of 0.02 Å, for phenyl rings in the case of the PPh₃ ligand, and for C₆F₄ groups in the case of the thiolate ligands. Finally, H atoms were placed in idealized positions and refined using a riding-model approximation (C—H = 0.93 Å) and fixed isotropic displacement parameters [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$]. The highest peak is located 1.33 Å from C101 and the deepest hole is located 1.16 Å from Os1.

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* and *MERCURY* (Version 1.4.1; Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXTL-Plus*.

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