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The oxotungsten(IV) complex $[WOCl(Ph_2PCH_2CH_2PPh_2)_2]PF_6\cdot CHCl_3$

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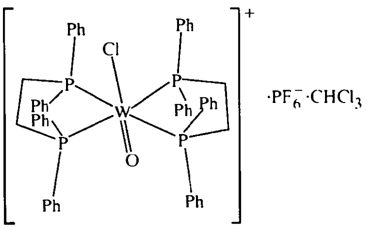
Abstract

Crystals of the title compound, chlorobis[ethylenebis(diphenylphosphine-*P*)]oxotungsten(IV) hexafluorophosphate trichloromethane solvate, $[WOCl(C_{26}H_{24}P_2)_2]$-$PF_6\cdot CHCl_3$, contain mononuclear tungsten complex molecules. The W atoms are octahedrally coordinated by two bidentate phosphine ligands and one Cl atom which is located *trans* to an O atom. The W—O distance is 1.851 (3) Å and the mean O—W—P angle is 94 (5)°. In contrast to the reported structure for an analogous cationic tungsten complex, the Cl- and O-atom positions do not show disorder.

Comment

As part of our investigations on tungsten clusters we have prepared the oxotungsten(IV) complex $[WOCl(Ph_2PCH_2CH_2PPh_2)_2]PF_6\cdot CHCl_3$, (1). A satisfactory synthesis of this compound was reported previously by Levason *et al.* (1977), and the complex has been characterized by spectroscopic, magnetic and conductivity measurements. In 1991, Cotton & Mandal reported an X-ray structural study of the tetraphenylborate salt of a similar cationic complex, $[WOCl(Ph_2PCH_2CH_2PPh_2)_2][BPh_4]$, (2), which displays disorder of the O- and Cl-atom positions. The need for more precise data and the general paucity of structural data on oxotungsten(IV) species has led to the work reported here.



(1)

Other structurally characterized mononuclear halogeno-oxotungsten(IV) complexes with phosphino ligands include $[WOCl(Me_2PCH_2CH_2PMe_2)_2]ClO_4$, (3), $[WOCl\{Me_2PCH_2(S)PMe_2\}_2]PF_6$, (4) (Cotton & Llusar, 1988), $[WOBr(Me_2PCH_2CH_2PMe_2)_2]Br\cdot 5H_2O$, (5) (Cotton *et al.*, 1989), and $[WOCl_2(PMePh_2)_2(CH_2{=}CH_2)]$, (6) (Su *et al.* 1986). One common feature of all these systems is the marked oxophilic character of tungsten, which is able to abstract oxygen not only from water but also from organic solvents.

The structures of the cations of (1) and (2) differ significantly in their W—O [1.851 (3) Å for (1) *versus* 1.68 (1) Å for (2)] and W—Cl bond distances [2.408 (1) Å for (1) *versus* 2.53 (1) Å for (2)]. These differences in W—*X* (*X* = O, Cl) bond lengths are likely to have their origin in the Cl/O disorder in (2), as has been discussed by Cotton & Mandal (1991). The importance of crystal purity in the determination of correct bond lengths has been pointed out by Yoon & Parkin (1991). Unusually long Mo—O bonds in oxochloro complexes of molybdenum(IV) have been attributed to disordered structures mainly caused by cocrystallization; this manifests itself in maxima near the oxo position in the difference electron-density maps (Yoon *et al.*, 1991). Difference electron-density maps for compound (1) show no excess electron density close to the O-atom position [in contrast to compound (2)], indicating the absence of disorder in the former crystal, even though a small amount of disorder cannot be ruled out. Also, refinement of the occupancy of the O- and Cl-atom positions results in values very close to unity.

The structure of (1) (Fig. 1) shares common features with those of (2), (3), (4) and (5), and it is closely related to that of (3) with the phosphinomethyl groups replaced by phenyl groups. Among these compounds, (1) has the longest W—O bond distance, 0.17 Å longer than the corresponding distance in (3), and 0.11 Å longer than that of (5). In our opinion, it is not likely that the long W—O bond in (1) is a result of electronic effects because of the similarities of the electronic properties of the ligands in all these compounds. We believe that it is rather the steric effect of the bulkier phosphine that causes the lengthening of the W—O bond.

Because a multiple bond generally occupies more space than a single bond [according to valence-shell electron-pair repulsion (VSEPR) theory], the terminal oxo group in these compounds exerts substantial steric

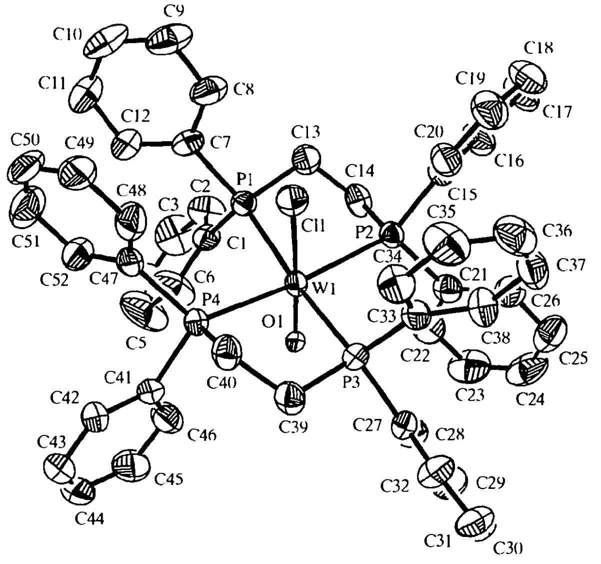


Fig. 1. The molecular structure of the complex ion $[WOCl(Ph_2PCH_2CH_2PPh_2)_2]^+$, with 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

influence, resulting in O—W—P angles larger than 90°. Compound (3) is the best example of this, with all O—W—P angles being larger than 95°, whereas steric or packing effects interfere with this demand in (1) [O—W—P angles: 88.4 (1), 92.0 (1), 95.7 (1) and 100.1 (1)°]. The smaller O—W—P angles in (1) compared with (3), together with the larger space required for a triple-bonded O atom compared with the single-bonded Cl atom, is the origin of the long W—O bond in (1). In spite of the longer W—O bond, the average P···O non-bonding distance in (1) is still 0.25 Å shorter than the van der Waals distance.

The W—Cl bond is 0.145 (3) Å shorter than that of (3) and even shorter than the *cis*-W—Cl bond of 2.444 (3) Å in (6). This also supports the idea of a weak or non-existent *trans* influence of the W—O bond in (1).

The conformation of the five-membered chelate rings of the coordinated phosphine ligands in compound (1) is λ/δ, while, in contrast, compound (2) presents a δ/δ conformation.

Experimental

WCl_4 (415 mg, 1.3 mmol) and NaHS (96 mg, 1.7 mmol) were suspended in THF (15 ml). Methanol (10 ml) was added to dissolve the sulfide. 1,2-Bis(diphenylphosphino)ethane (dppe; 508 mg, 1.3 mmol) was introduced and the reaction mixture refluxed for 2 h under nitrogen. After the reaction mixture had cooled to room temperature, a green precipitate was filtered off. The solvent was removed, the residue dissolved in CH_2Cl_2/hexane (1:1) and absorbed on a silica-gel column. After the column had been washed with acetone, the product was eluted with an acetone/methanol mixture (1:1). The solution was taken to dryness and dissolved in methanol. Addition of KPF_6 precipitated the title compound which was filtered and recrystallized from CH_2Cl_2/hexane [yield: *ca* 40% (based on W) and 80% (based on dppe)]. Crystals suitable for X-ray diffraction studies were grown by slow diffusion of hexane into a chloroform solution of the product.

Crystal data

$[WOCl(C_{26}H_{24}P_2)_2]PF_6 \cdot CHCl_3$
$M_r = 1296.491$
Triclinic
$P\bar{1}$
$a = 11.684 (2)$ Å
$b = 14.943 (3)$ Å
$c = 16.749 (3)$ Å
$\alpha = 105.79 (1)°$
$\beta = 106.85 (1)°$
$\gamma = 91.36 (1)°$
$V = 2676 (1)$ Å^3
$Z = 2$
$D_x = 1.609$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 46 reflections
$\theta = 2.2–22.2°$
$\mu = 2.566$ mm^{-1}
$T = 293 (2)$ K
Prism
0.25 × 0.10 × 0.02 mm
Orange

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: ψ scan (*SHELXTL-Plus*; Sheldrick, 1990)
$T_{min} = 0.513$, $T_{max} = 0.989$
13 677 measured reflections
11 889 independent reflections

9322 reflections with $F > 4\sigma(F)$
$R_{int} = 0.020$
$\theta_{max} = 28°$
$h = -14 \rightarrow 1$
$k = -18 \rightarrow 18$
$l = -22 \rightarrow 22$
2 standard reflections every 98 reflections intensity decay: none

Refinement

Refinement on *F*
$R = 0.046$
$wR = 0.048$
$S = 1.421$
9322 reflections
644 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F) + 0.0001F^2]$
$(\Delta/\sigma)_{max} = 0.06$
$\Delta\rho_{max} = 1.75$ e Å^{-3}
$\Delta\rho_{min} = -1.31$ e Å^{-3}
Extinction correction: none
Scattering factors from *SHELXTL-Plus* (Sheldrick, 1990)

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

W1—P1	2.554 (2)	W1—P4	2.538 (2)
W1—P2	2.550 (2)	W1—Cl1	2.408 (1)
W1—P3	2.544 (2)	W1—O1	1.851 (3)
P1—W1—P2	79.6 (1)	P3—W1—Cl1	86.4 (1)
P1—W1—P3	172.1 (1)	P4—W1—Cl1	78.7 (1)
P2—W1—P3	99.1 (1)	P1—W1—O1	92.0 (1)
P1—W1—P4	99.9 (1)	P2—W1—O1	88.4 (1)
P2—W1—P4	171.5 (1)	P3—W1—O1	95.7 (1)
P3—W1—P4	80.2 (1)	P4—W1—O1	100.1 (1)
P1—W1—Cl1	86.0 (1)	Cl1—W1—O1	177.4 (1)
P2—W1—Cl1	92.8 (1)		

The structure was solved by direct methods (*SHELXTL-Plus*; Sheldrick, 1990). The remaining atoms were obtained from difference Fourier maps following least-squares cycles. After isotropic refinement of this model, H atoms were added at idealized positions and allowed to ride on their parent atoms with one common isotropic displacement parameter per group. The largest peak in the final difference Fourier map (1.75 e Å^{-3}) is located 0.93 Å from the W1 atom.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1990). 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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1303). Services for accessing these data are described at the back of the journal.

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Zinc(II) complexes of bidentate Schiff base ligands containing methoxyphenyl and nitrophenyl groups

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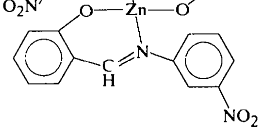
Abstract

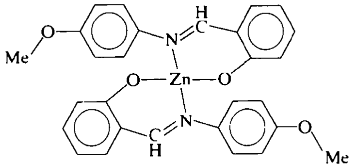
In the title compounds, bis[2-(3-nitrophenylnitrilomethylidyne)phenolato-*N*,*O*]zinc(II), [Zn($C_{13}H_9N_2O_3$)$_2$], and bis[2-(3-methoxyphenylnitrilomethylidyne)phenolato-*N*,*O*]zinc(II), [Zn($C_{14}H_{12}NO_2$)$_2$], the tricilinic unit cell contains two inversion-related molecules. In both compounds, the Zn atom is in a slightly distorted tetrahedral coordination involving O and N atoms of two bidentate ligands. The dihedral angle defined by the two chelate rings is 98.09 (4)° for the methoxyphenyl complex and 98.05 (7)° for the nitrophenyl complex. The molecules are crosslinked *via* intermolecular hydrogen bonds.

Comment

Metal complexes formed with *O*,*N*-type bidentate Schiff base ligands have a variety of coordination possibilities resulting in compounds with interesting properties. For instance, among the zinc compounds there are monomeric complexes in which the Zn atom is tetrahedrally coordinated (Frasson & Panattoni, 1961; Sogo *et al.*, 1988; Sakiyama *et al.*, 1990; Tatar *et al.*, 1999), as well as dimeric complexes with phenolate bridges and a trigonal-bipyramidal coordination around each Zn atom, as observed in (*N*-methylsalicylaldiminate)zinc(II) (Orioli *et al.*, 1965). We synthesized two new zinc complexes, namely, bis[2-(3-nitrophenylnitrilomethylidyne)phenolato-*N*,*O*]zinc(II), (1), and bis[2-(3-methoxyphenylnitrilomethylidyne)phenolato-*N*,*O*]zinc(II), (2), and report their structures here.



(1)



(2)

In both compounds, the structure consists of asymmetric monomers (Fig. 1), which are related by an inversion center of the triclinic unit cell and crosslinked by a set of intermolecular hydrogen bonds. The tetrahedral coordination around the Zn^{2+} ion, involving two phenolate O and two imine N atoms of two Schiff base ligands, is slightly distorted. The coordination bond angles are in the range 97.38 (6)–123.62 (7)° for the methoxyphenyl complex and in the range 95.5 (1)–126.1 (1)° for the nitrophenyl complex. The distortion from ideal tetrahedral geometry is a consequence of the limited opening of the bidentate ligands, which reduces the chelating O—Zn—N angle, and also steric repulsion