Synthesis and Crystal Structure of Tetraphenylarsonium Pentachlorocarbonylosmate(IV), (Ph₄As)[OsCl₅(CO)]

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Pentachloromonocarbonylosmate(IV), Crystal Structure, Positional Disorder

The structure of tetraphenylarsonium pentachlorocarbonylosmate(IV), (Ph₄As)[OsCl₅(CO)], the first example of a halogenocarbonyl complex with osmium in the oxidation state +IV, has been determined at 208 K by single crystal X-ray diffraction: tetragonal, space group P4/n with a = 12.821 Å, c = 8.084 Å, Z = 2. There are short intermolecular contacts between neighbouring anions along the tetragonal axis c and unusually large displacement ellipsoids of the carbonyl group and the four equatorial Cl ligands arising from a positional disorder of the complex anion. By analogy with a variety of reported structures of the (Ph₄As)[RuNCl₄] structure type this is attributed to the close packing of the cation sublattice. Compared to other monocarbonylosmates the Os-C bond of 1.94(2) Å is extraordinarily long while the bond between Os and the trans coordinated Cl ligand of 2.286(3) Å is rather short.

Introduction

In the last decades halogenocarbonyl metallates have been objects of intense studies. Usually only low oxidation states of the central atom were reported. In contrast to halogenonitrosyllosmates [1], highly oxidized halogenocarbonylosmates have been characterized until now only by their spectroscopic and electrochemical properties [2, 3]. To our knowledge the present report on an X-ray structure of a halogenocarbonyl compound is the first for osmium in the oxidation state +IV.

Experimental

a) Synthesis

(Ph₄As)[OsCl₅(CO)] (1) has been synthesized by reaction of 10 ml of a nearly saturated solution of trans-(Ph₄As)[OsBr₅(CO)], in CH₂Cl₂ with Cl₂ gas at 298 K [2]. After a few minutes the initially pink solution turned to dark brown. The reaction was stopped after 3 h and single crystals of (1) were grown by cooling the solution down to -35°C. Solutions of the compound are very sensitive to moisture, but the black crystals are rather stable when stored in a dry atmosphere.

b) X-ray structure determination

A single crystal of 1 was embedded in perfluorinated polyether of high viscosity and mounted on a glass capillary. The data for the structure determination were measured with an Enraf-Nonius CAD-4 Turbo four-circle diffractometer [4] at 208 K. Lattice parameters were calculated from 25 reflections in the 2θ range 6.34° - 11.50°. Three standard reflections were measured every 250 min, the intensity decay was 6.9%. After data reduction, absorption correction [5, 6] and determination of the space group on the basis of systematic absences the structure was solved by direct methods [7]. Parameters of non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in calculated positions and restrained to their parent site by a riding model [8].

Crystal data, data collection parameters and results of the least squares refinement are given in Table I. The atomic parameters are listed in Table II, selected geometric parameters in Table III. Further details, also of the split site refinement test of the carbonyl group, are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany on quoting the registry number CSD 407301.

Results and Discussion

Tetraphenylarsonium pentachlorocarbonylosmate(IV) crystallizes in space group P4/n. Columns along the short axis c are formed by the tetrahedral cations as well as by the hexacoordinated anions, respectively. In first order the Cl - Os - (CO) fragment resides on the fourfold rotational axis with the local symmetry C₄ᵥ (4mm). The structure corresponds to the (Ph₄As)[RuNCl₄] structure type
Fig. 1. View of the structure of \((\text{Ph}_4\text{As})[\text{OsCl}_5(\text{CO})]\) showing 50% probability displacement ellipsoids (H atoms of interest as spheres of arbitrary size). Symmetry codes: (i) \(x, y, z + 1\); (ii) \(x, y, z - 1\); (iii) \(1/2 + y, 1 - x, 1 - z\); (iv) \(1/2 - y, x, z\).

Table I. Crystal data for \((\text{Ph}_4\text{As})[\text{OsCl}_5(\text{CO})]\), data collection and refinement parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>(C_{25}) H_{20} As Cl_{5} O Os</td>
</tr>
<tr>
<td>Formular weight [g mol(^{-1})]</td>
<td>778.78</td>
</tr>
<tr>
<td>Crystal system</td>
<td>tetragonal</td>
</tr>
<tr>
<td>Space group</td>
<td>(P4/n)</td>
</tr>
<tr>
<td>(a) [(\text{Å})]</td>
<td>12.821(2)</td>
</tr>
<tr>
<td>(c) [(\text{Å})]</td>
<td>8.084(1)</td>
</tr>
<tr>
<td>Cell volume [(\text{Å}^3)]</td>
<td>1328.8(3)</td>
</tr>
<tr>
<td>(Z)</td>
<td>2</td>
</tr>
<tr>
<td>Density [g (\text{cm}^\text{-3})]</td>
<td>1.946</td>
</tr>
<tr>
<td>Crystal dimensions [mm]</td>
<td>0.20 (\times) 0.25 (\times) 0.30</td>
</tr>
<tr>
<td>Absorption coeff. (\mu) [mm(^{-1})]</td>
<td>6.553</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>(\Psi)-scans</td>
</tr>
<tr>
<td>Temperature [K]</td>
<td>208(2)</td>
</tr>
<tr>
<td>Radiation [(\text{pm})]</td>
<td>MoK(\alpha), (\lambda = 71.069)</td>
</tr>
<tr>
<td>Scan mode</td>
<td>(\omega)-2(\theta)</td>
</tr>
<tr>
<td>2(\theta) range [(^\circ)]</td>
<td>4.5 - 50.0</td>
</tr>
<tr>
<td>(h, k, l) range</td>
<td>(0 \rightarrow 15, 0 \rightarrow 15, 0 \rightarrow 9)</td>
</tr>
<tr>
<td>Measured / independent reflections</td>
<td>1282 / 1172</td>
</tr>
<tr>
<td>Observed reflections [(I &gt; 2\sigma(I))]</td>
<td>986 ((R_{int} = 0.0293))</td>
</tr>
<tr>
<td>Refined parameters</td>
<td>79</td>
</tr>
<tr>
<td>Goodness-of-fit on (F^2)</td>
<td>1.080</td>
</tr>
<tr>
<td>Residual electron density [e/(\text{Å}^3)]</td>
<td>(-0.829) (\Delta\rho_{max}); (-1.104) (\Delta\rho_{min})</td>
</tr>
<tr>
<td>(wR(F^2))</td>
<td>0.0731</td>
</tr>
<tr>
<td>(R(F^2 &gt; 2\sigma(F^2)))</td>
<td>0.0280</td>
</tr>
</tbody>
</table>

Table II. Positional parameters (\(\times 10^4\)) and equivalent isotropic displacement parameters \(U_{eq} [\text{Å}^2 \times 10^3]\) of \((\text{Ph}_4\text{As})[\text{OsCl}_5(\text{CO})]\).

<table>
<thead>
<tr>
<th>Atom</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>(U_{eq})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os</td>
<td>2500</td>
<td>2500</td>
<td>3254(1)</td>
<td>37(1)</td>
</tr>
<tr>
<td>Cl1</td>
<td>2500</td>
<td>2500</td>
<td>426(4)</td>
<td>62(1)</td>
</tr>
<tr>
<td>Cl2</td>
<td>4233(1)</td>
<td>1984(2)</td>
<td>3286(3)</td>
<td>76(1)</td>
</tr>
<tr>
<td>C</td>
<td>2500</td>
<td>2500</td>
<td>565(3)</td>
<td>150(10)</td>
</tr>
<tr>
<td>O</td>
<td>2500</td>
<td>2500</td>
<td>699(2)</td>
<td>310(20)</td>
</tr>
<tr>
<td>As</td>
<td>7500</td>
<td>2500</td>
<td>5000</td>
<td>30(1)</td>
</tr>
<tr>
<td>Cl1</td>
<td>6412(4)</td>
<td>2063(4)</td>
<td>6458(7)</td>
<td>31(1)</td>
</tr>
<tr>
<td>Cl2</td>
<td>5975(4)</td>
<td>1084(4)</td>
<td>6339(8)</td>
<td>40(1)</td>
</tr>
<tr>
<td>C3</td>
<td>5234(5)</td>
<td>1614(5)</td>
<td>7580(9)</td>
<td>53(2)</td>
</tr>
<tr>
<td>C4</td>
<td>4948(5)</td>
<td>1459(5)</td>
<td>8738(9)</td>
<td>53(2)</td>
</tr>
<tr>
<td>C5</td>
<td>5395(5)</td>
<td>2430(5)</td>
<td>8857(9)</td>
<td>52(2)</td>
</tr>
<tr>
<td>C6</td>
<td>6132(5)</td>
<td>2740(5)</td>
<td>7727(8)</td>
<td>45(2)</td>
</tr>
</tbody>
</table>

Table III. Selected geometric parameters [\(\text{Å}, ^\circ\)] of \((\text{Ph}_4\text{As})[\text{OsCl}_5(\text{CO})]\).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length [Å]</th>
<th>Angle [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os - C</td>
<td>1.94(2)</td>
<td>Cl' - O</td>
</tr>
<tr>
<td>Os - Cl1</td>
<td>2.286(3)</td>
<td>C11 - H4ii</td>
</tr>
<tr>
<td>Os - Cl2</td>
<td>2.319(2)</td>
<td>C12 - H4ii</td>
</tr>
<tr>
<td>As - Cl1</td>
<td>1.910(5)</td>
<td>C12 - H3iii</td>
</tr>
<tr>
<td>C - O</td>
<td>1.08(2)</td>
<td>C12v - H3iii</td>
</tr>
<tr>
<td>C - Os - Cl2</td>
<td>89.36(7)</td>
<td>C11 - Os - Cl2</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) \(x, y, z + 1\); (ii) \(x, y, z - 1\); (iii) \(1/2 + y, 1 - x, 1 - z\); (iv) \(1/2 - y, x, z\).

displacement ellipsoids of the four equatorial Cl ligands and the carbonyl group are very large (Table II) and those of the equatorial Cl ligands unusually inclined (Fig. 1).

Müller and El-Kholi [13] have explained this phenomenon by a positional disorder model which can be applied also to the present structure. Ligand C11 is fixed on the fourfold axis by close contacts to phenyl groups of the four adjacent cations [C11...H4ii: 3.05(1) Å; (ii): \(x, y, z - 1\)]. Since the remaining part of the anion is spatially less limited, it is statistically tilted away from the c-axis. This is caused by short intermolecular anion - anion contacts along axis c arising from the structure determining close packing of the cation sublattice. The intermolecular Cl1...O'' distance of 2.78(2) Å is significantly shorter than the sum of the v. d. Waals radii (3.2 - 3.4 Å [15]). The displacement parameters of the O atom \([U_{11} = U_{22} = 0.45(3) \text{ Å}^2]\) (Table IV) correspond to a circle of about 1.3 Å in diameter for the locations of possible split sites. Despite of high correlations it was possible to perform an
Table IV. Anisotropic displacement parameters $U_{ij}$ [Å$^2$ x $10^3$] of (Ph$_4$As)[OsCl$_5$(CO)].

<table>
<thead>
<tr>
<th></th>
<th>$U_{11}$</th>
<th>$U_{22}$</th>
<th>$U_{33}$</th>
<th>$U_{23}$</th>
<th>$U_{13}$</th>
<th>$U_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os</td>
<td>41(1)</td>
<td>41(1)</td>
<td>29(1)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cl1</td>
<td>77(2)</td>
<td>77(2)</td>
<td>33(2)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cl2</td>
<td>48(1)</td>
<td>60(1)</td>
<td>120(2)</td>
<td>-1(1)</td>
<td>-35(1)</td>
<td>5(1)</td>
</tr>
<tr>
<td>C</td>
<td>200(20)</td>
<td>200(20)</td>
<td>41(12)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O</td>
<td>450(30)</td>
<td>450(30)</td>
<td>20(9)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>As</td>
<td>31(1)</td>
<td>31(1)</td>
<td>28(1)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The anisotropic refinement with four split sites for C and O as a test for the disorder model. As the split sites of O were refined to positions 0.7 Å from the fourfold axis, the distance between adjacent anions increased by about 0.1 Å, but the refinement parameters (Goof, R) are virtually the same as for the structure model presented in Fig. 1 and Table I - IV. These results proof the concept of Müller and El-Kholi qualitatively. Since the bond lengths given in Table III are not corrected for the tilting, distances to the atoms with unusually large displacement ellipsoids appear systematically too short. Nevertheless the Os - C bond of 1.94(2) Å is still considerably longer than the data reported for halogenocarbonyl compounds with osmium in the oxidation state +III ranging from 1.80 to 1.86 Å [16 - 20]. This reflects the expected weakening of the Os - C bond due to a diminished back donation from the hard Os(IV) to the soft carbonyl group. Accordingly the IR band assigned to the Os-C stretching vibration is shifted by 29% from 543 to 388 cm$^{-1}$ [2] and the calculated valence force constant decreases by 44% [20] compared to the isostructural complex of Os(III). The Os - Cl bond of 2.286(3) Å appears to be compressed in spite of the strong trans influence of the carbonyl group. The tetraphenylarsonium cation shows the expected geometric and displacement parameters.

Acknowledgments

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