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Syntheses, structures and DFT study of $[W(CO)_5(Ph_2SbX)]$ $X = Cl, Br, I$

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Abstract

The complexes $[W(CO)_5(Ph_2SbX)]$, X = Cl (**1**), Br (**2**) and I (**3**) were prepared by reaction of $[W(CO)_5(\text{tetrahydrofuran})]$ with Ph_2SbX. The structures of **1**–**3** were studied by X-ray diffraction. In the crystals there are weak contacts between the oxygen atoms of the CO ligands and antimony atoms of neighbouring molecules. DFT calculations were carried out for **1** using gradient corrected functional B3LYP. The bonding between Ph_2SbCl and the $W(CO)_5$ fragment in **1** was analysed using charge decomposition analysis.

Keywords: Antimony; Tungsten; X-ray structure; DFT

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1. Introduction

Pentacarbonyl metal complexes with diorganoantimony halide ligands of the type $[M(CO)_5(R_2SbX)]$ possess a functional group at antimony and hence they can be useful as antimony reagents with protection by the metal carbonyl fragment. The inspection of their crystal structures and theoretical calculations allow to study the effect of coordination on the geometry of the R_2SbX unit. Several complexes of this type have been synthesised [1–5]; none of them was studied by X-ray diffraction. We chose the series $[W(CO)_5(Ph_2SbX)]$, X = Cl (**1**), Br (**2**) and I (**3**) for an inspection of the crystal structures and selected **1** for a study at the DFT level. The synthesis and characterisation of **1** [1] and the crystal structures of the free ligands Ph_2SbX (X = Cl [6], Br [7], I [8]) were reported before.

2. Results and discussion

$[W(CO)_5(Ph_2SbCl)]$ (**1**) was prepared by the exchange reaction between $[W(CO)_5(THF)]$ (THF = tetrahydrofuran) and diphenylantimony chloride as described by Wieber and Graf [1]. An analogous procedure led to $[W(CO)_5(Ph_2SbX)]$ [X = Br (**2**), I (**3**)]. Yellow green (**1**) or yellow (**2**, **3**) single crystals were obtained by cooling solutions in petroleum ether. The crystals are air stable and well soluble in organic solvents. Also thermally **1**–**3** are relatively stable. They melt without decomposition above 80 °C but become slowly brown after further heating of the liquids. The structures of **1**–**3** were determined by single crystal X-ray diffraction. The molecules are composed of pyramidal Ph_2SbX units coordinated through the antimony atoms to tetragonal pyramidal $W(CO)_5$ fragments. The phenyl groups adopt a propeller like arrangement. As a representative example the structure of **3** is depicted in Fig. 1. Relevant bond lengths and bond angles of **1**–**3** and of the non-coordinated diphenylantimony halides are listed in Table 2.

The Sb–W bonds in **1**: 2.7184(10), **2**: 2.7243(8), **3**: 2.7256(7) Å are slightly shorter than the corresponding

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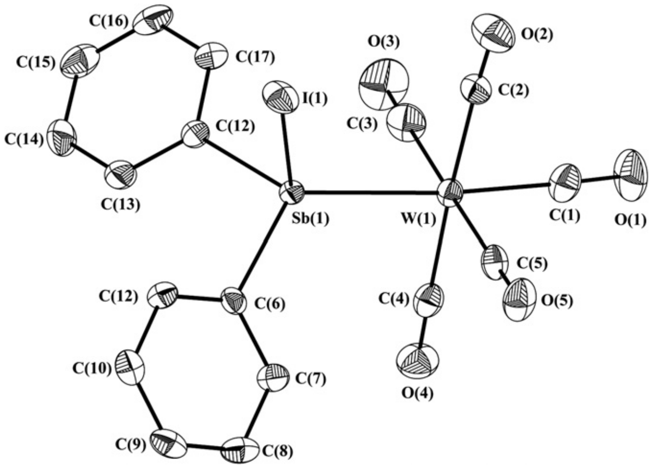

Fig. 1. ORTEP style representation at 50% probability and the numbering scheme of [W(CO)$_5$(Ph$_2$SbI)] (**3**).

bonds in [W(CO)$_5$(Ph$_3$Sb)] 2.745(1) Å [9], [{W(CO)$_5$}$_n$-{(Ph$_2$Sb)$_2$CH$_2$}], $n = 1$; 2.743(1), $n = 2$; 2.756(2) Å [10], or [{W(CO)$_5$}$_2$(Ph$_2$Sb$_2$)] 2.749(1) Å [11]. The values for the W–C bond lengths in **1**–**3** range from 1.989(8) to 2.056(6) Å. The W–C bonds *trans* to the Ph$_2$SbX ligands are in average 3% (0.048 Å in **1**, 0.047 Å in **2** and 0.044 Å in **3**) shorter than those in *cis* positions. The C–O bond lengths lie between 1.114(8) and 1.154(11) Å close to the values encountered in related complexes [9–11]. The Sb–C and the Sb–halogen bonds are a little shorter in the complexes than in the free ligands. A remarkable result of the coordination is the widening of the C–Sb–C and C–Sb–X bond angles. The sum of the bond angles, i. e. C–Sb–C and C–Sb–X at antimony is between 8° and 11° larger in the complexes **1**–**3** than in the free ligands.

Interesting differences emerge also when the packing of **1**–**3** in the crystal is inspected. Crystals of **1** contain pairs of molecules (Fig. 2), with contact distances of 3.451(8) Å between oxygen atoms of carbonyl groups and antimony atoms of the neighbouring molecules. These distances are close to the sum of van der Waals radii of antimony and oxygen [$\sum_{\mathrm{rvdW}}$(Sb, O) 3.52 Å] [12]. Although it appears that the intermolecular Sb···O contacts are very weak it is remarkable that the oxygen atoms of the neighbouring molecules occupy positions *trans* to the Sb–Cl bonds (Cl–Sb···O 172.39(14)°). This pattern is typical for Lewis-acid–base interactions between diorgano antimony halides and donor molecules [13]. In an analogous manner also the dimeric association of **1** in the crystal may result from a very weak intermolecular Lewis-acid–base interaction, which leads to the bridging coordination of the CO molecule between tungsten and antimony. The interaction M–CO···M′ in **1** leads to an elongation of the C–O bond. In fact the bond length of the CO group involved in the intermolecular interaction with 1.154 Å is the longest encountered in **1**–**3**. Examples of complexes with a CO group coordinated to a second metal centre are well known [14,15]. Bridging CO groups between a transition metal and a p block elements were reported in the structures of [{η-C$_5$H$_5$W(CO)$_3$(AlMe$_2$)}$_2$] (C–O 1.18(3), CO···Al 1.793(18) Å) [16] and [Co(Ph$_3$P)$_2$(CO)$_3$BEt$_3$] (C–O 1.157(4), CO···B 1.601(5) Å) [17]. In crystals of **1** there are also weak intermolecular contacts between the oxygen atom of the bridging CO group and the *ortho* hydrogen atoms of the closest phenyl ring. The contact distance (H···O 2.641 Å) is close to the sum of van der Waals radii of the respective elements [$\sum_{\mathrm{vdW}}$(H, O) ca. 2.72 Å].

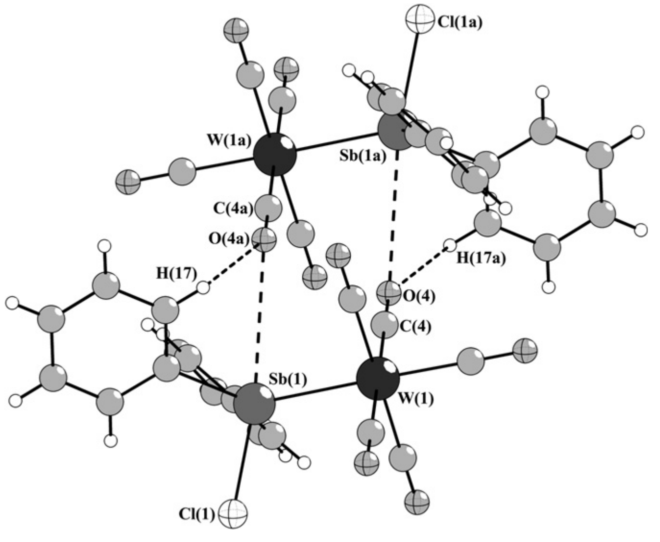

Fig. 2. Dimeric association of [W(CO)$_5$(Ph$_2$SbCl)] (**1**).

Weak intermolecular Sb···O contacts [3.368(5) Å] exist also in crystals of **2**. The Br–Sb···O angle of 156.58(9)° indicates a considerable deviation from an ideal *trans* arrangement. Through the Sb···O interactions the molecules of **2** are arranged to infinite chains. Between the chains there are weak contacts (H···O 2.64 Å) connecting the oxygen atoms of carbonyl groups and *para*-hydrogen atoms of phenyl groups. A section of two chains in the crystals of **2** is shown in Fig. 3.

Also the molecules of **3** are arranged in infinite chains through weak intermolecular interactions between antimony and oxygen atoms of carbonyl groups. The shortest Sb···O distance is 3.548(6) Å, right at the van der Waals limit. The angle I–Sb···O is 155.65(11)°. Besides the weak interactions listed above the molecular units are connected through a net of interactions between the hydrogen atoms of the phenyl groups and the oxygen atoms of the carbonyl groups.

For a better understanding of the coordinative bonding in **1** theoretical studies using DFT, NBO and CDA methods were carried out. The DFT and NBO calculations were performed for the free ligand, Ph$_2$SbCl and for the complex **1**. In particular, we wanted to explain the experimentally observed increase in the sum of bond angles at antimony in the Ph$_2$SbCl unit as a result of the complexation. The calculated geometrical parameters are in good agreement with the experimental data. The bond lengths and bond angles are listed in Table 1. The former