Note

The crystal structure of a chelate silver(I) complex: $\{Ag[Ph_2P(CH_2)_2SCH_2CH_3]_2\}ClO_4$

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Abstract

A single crystal of the $\{Ag[Ph_2P(CH_2)_2SCH_2CH_3\}ClO_4$ complex, $[Ag(PSEt)_2]ClO_4$, has been isolated from anhydrous propylene carbonate solution containing $AgClO_4$ and the ligand in a 1:2 ratio. An X-ray diffraction analysis, carried out by adopting the heavy-atom method, shows that no solvent molecules are present in the adduct, enabling the PSEt ligand to behave as a chelating agent, both P and S atoms being coordinated to the metal ion. The coordination geometry around silver(I) can be described as a distorted tetrahedron with a P–Ag–P′ angle of 148.9(1)°, this is most likely due to the repulsion between two phenyl rings (C4...C4′ = 3.96 Å) which has the further consequence of lowering the S–Ag–P bond angle to 82.5(1)°.

Key words: Crystal structures, Silver complexes, Chelate phosphine ligand complexes

Introduction

In recent years increasing interest has been devoted to the chemistry of phosphines and their metal complexes [1]. In particular, the chemistry of transition metal complexation with phosphines which also contain other donor atoms, such as N or O, has received intensive study primarily for their application as hydrogenation catalysts [2–7].

Recent thermodynamic studies [8] on the complexation of the monovalent d^{10} acceptor silver(I) with mixed $Ph_2P(CH_2)_nSR$ ligands ($n = 1$, R = Me, Ph; $n = 2$, R = Me, Et, Ph) in dimethyl sulfoxide (dmso) show that, in this solvent, all ligands behave as monodentate coordinating silver(I) through the phosphorus atom. As the thioether groups are known to be stronger donors than dmso [9, 10], the reason why these groups do not coordinate silver(I) in dmso solution has been inferred to the larger activity of the solvent which compensates for the slightly stronger donors properties of the thioether functions [8].

We have recently undertaken a thermodynamic investigation on the complex formation between silver(I) and P-S donor ligands in anhydrous propylene carbonate, a poor coordinating solvent toward silver(I) [11]. Preliminary results indicate that in this solvent $Ph_2P(CH_2)_2SR$ ligands (R = Me, Et, Ph) behave as bidentate, at least in ML_2 complexes.

To gain information on the possible structure of ML_2 complexes, we have isolated and analyzed by X-ray diffraction technique a single crystal of the $\{Ag[Ph_2P(CH_2)_2SCH_2CH_3]_2\}ClO_4$ complex, $[Ag(PSEt)_2]ClO_4$, which has been chosen as representative of a series of ML_2 complexes formed by the above mentioned ligands of general formula $Ph_2P(CH_2)_2SR$.

Experimental

Chemicals

Anhydrous $AgClO_4$ was obtained by heating under vacuum at 50 °C and for several days, the solid obtained by crystallization from benzene of an $AgClO_4 \cdot H_2O$ (Fluka puriss.) solution from which water had been previously removed by a Dean and Stark distilling receiver [12]. Propylene carbonate (Fluka > 99%) was distilled at reduced pressure from CaH_2. The middle 60% fraction was collected and redistilled under identical conditions [13]. The ligand $Ph_2P(CH_2)_2SCH_2CH_3$ (PSEt) was prepared according to methods reported in the literature [14] and was doubly recrystallized from CH_2Cl_2–EtOH. White crystals of the complex $[Ag(PSEt)_2]ClO_4$ were grown by slow diffusion of diethyl ether vapors into an anhydrous propylene carbonate solution containing $AgClO_4$ and the ligand in a 1:2 ratio.

Crystal data

$AgS_2P_2C_{32}H_{38}ClO_4$. *Anal.* Found: C, 50.75; H, 5.11. Calc.: C, 50.84; H, 5.07%. Formula weight 756.05, orthorhombic, *Fdd*2, $a = 14.019(2)$, $b = 32.037(3)$, $c = 15.107(2)$ Å, $V = 6785(1)$ Å^3, $Z = 8$, $D_x = 1.48$ Mg m^{-3}, λ(Mo Kα) = 0.71069 Å, $\mu = 9.1$ cm^{-1}, F(000) =

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3104, room temperature, crystal dimensions $0.3 \times 0.3 \times 0.1$ mm, 1549 reflections measured with the ω scan in the range $6 < 2\theta < 50°$. Absorption correction was applied with the aid of ψ-scan data.

X-ray analysis

The structure was solved with Shelxs86 [15] adopting the heavy-atom method. Refinement was carried out with Shelx76 [16] with all heavy atoms and oxygens allowed to vibrate anisotropically. Hydrogen atoms were inserted at calculated positions. Unit weights were adopted throughout the refinement procedure. The final disagreement factor is $R = 0.037$ with 112 refinable parameters and 1327 reflections with $I > 3\sigma(I)$. The maximum shift/error ratio is 0.52.

Results and discussion

Fractional atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1 while a description of the molecular geometry is given in Table 2. An arbitrary view of the $[Ag(PSEt)_2]^+$ cation and of the ClO_4^- anion with the numbering scheme is shown in Fig. 1

The lack of solvent molecules in the adduct is not surprising considering the weak affinity of propylene carbonate toward silver(I) [11]. On the other hand the sulfur atom, which in dmso solutions is not coordinated [8], in this case is bonded to Ag^+, as a consequence of the poor competitive action of propylene carbonate. This enables the PSEt ligand to behave as a chelating agent, both P and S atoms being coordinated to the central metal ion.

TABLE 1 Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters of all non-hydrogen atoms for $[Ag(PSEt)_2]ClO_4$

Atom	x	y	z	B
Ag	0	0	9215(1)	3.4(1)
Cl	0	0	4493(2)	4.8(3)
S	1554(2)	154(1)	8217(2)	4.2(2)
P	927(1)	−617(1)	9650(1)	2.9(1)
O1	3019(12)	7763(5)	2493(12)	18.6(23)
O2	1872(8)	7729(3)	1445(8)	11.7(13)
C1	2140(6)	−357(3)	8275(6)	4.2(2)
C2	2131(5)	−514(2)	9232(6)	3.6(1)
C3	1145(5)	−756(2)	803(5)	2.9(1)
C4	947(7)	−459(3)	1451(6)	4.3(2)
C5	1116(7)	−549(3)	2339(7)	5.3(2)
C6	1470(8)	−933(3)	2582(8)	5.8(2)
C7	1687(7)	−1225(3)	1941(7)	5.1(2)
C8	1521(6)	−1144(3)	1049(6)	3.8(2)
C9	1381(7)	201(3)	7042(7)	5.2(2)
C10	885(9)	603(4)	6846(10)	7.5(3)
C11	1203(7)	−1401(3)	8830(6)	4.6(2)
C12	855(8)	−1761(3)	8388(7)	5.5(2)
C13	−80(8)	−1807(3)	8229(7)	5.4(2)
C14	−724(8)	−1505(3)	8495(7)	5.1(2)
C15	−410(6)	−1150(3)	8942(6)	4.0(2)
C16	566(5)	−1098(2)	9105(5)	3.1(1)

TABLE 2. Molecular dimensions for $[Ag(PSEt)_2]ClO_4$

Selected bond lengths (Å)	
Ag–S	2.694(2)
Ag–P	2.456(2)
Cl–O1	1.345(17)
Cl–O2	1.414(12)
S–C1	1.832(9)
S–C9	1.799(10)
P–C2	1.832(8)
P–C3	1.823(8)
P–C16	1.818(7)
C1–C2	1.531(13)
C9–C10	1.494(15)
Selected bond angles (°)	
P–Ag–P′	148.9(1)
S–Ag–P′	115.5(1)
S–Ag–P	82.5(1)
S–Ag–S′	112.0(1)
O2–Cl–O2′	108.4(7)
O1–Cl–O2′	108.5(8)
O1–Cl–O1′	111.6(10)
O1–Cl–O2	109.9(8)
C1–S–C9	100.6(4)
C3–P–C16	105.8(3)
C2–P–C16	104.7(3)
C2–P–C3	102.6(4)
S–C1–C2	109.5(6)
P–C2–C1	113.2(5)
S–C9–C10	109.3(8)
P–C3–C8	122.3(6)
P–C3–C4	118.1(6)
P–C16–C15	116.9(6)
P–C16–C11	123.4(6)
Selected torsion angles (°)	
Ag–S–C9–C10	71.9(0.8)
Ag–S–C1–C2	−45.3(0.6)
C1–S–C9–C10	179.1(0.8)
C9–S–C1–C2	−165.7(0.6)
Ag–P–C16–C11	142.0(0.6)
Ag–P–C3–C4	−13.3(0.8)
Ag–P–C2–C1	−46.7(0.6)
C3–P–C16–C11	−79.7(0.8)
C2–P–C3–C4	103.3(0.7)
C16–P–C2–C1	73.8(0.6)
S–C1–C2–P1	65.0(0.7)

Primed atoms are obtained through the operation $\bar{x}$, $\bar{y}$, z

The coordination geometry around silver(I) may be described as a very distorted tetrahedron with a P–Ag–P′ angle of 148.9(1)°, by far higher than the theoretical value of 109.5° and higher than those already found in $(PPh_3)Ag_2MoS_4 \cdot 0.8CH_2Cl_2$ [17] and $Ag_2[S_2C_2(CN)_2]$-$[PPh_3]_4$ [18] compounds. This is certainly due to the repulsion between two phenyl rings (C4 - - - C4′ = 3.96 Å) which has the further consequence of lowering the S–Ag–P bond angle to 82.5(1)°. Ag–P and Ag–S

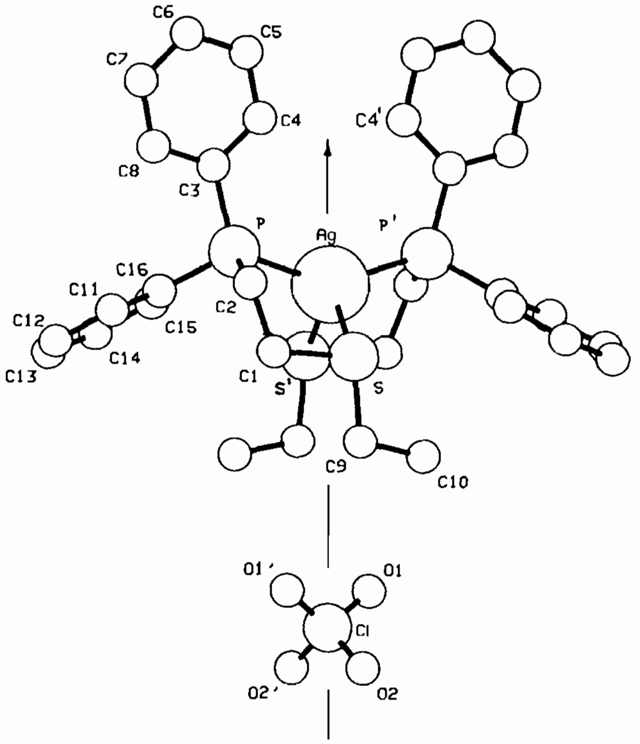

Fig. 1. Arbitrary view of the $[Ag(PSEt)_2]^+$ cation and of the ClO_4^- anion, both located on a two-fold axis.

bond lengths (2.456(2) and 2.694(2) Å, respectively) are both within the expected range being comparable with those observed in other silver compounds [17–21].

Supplementary material

Tables of anisotropic temperature factors, hydrogen coordinates, and observed and calculated structure factors are available from the authors on request.

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