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Unexpected diastereoisomeric-trimers in the crystalline structure of triflatetriphenylphosphinesilver(I)

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Abstract

The synthesis and spectroscopic properties of $[Ag_3(O_3SCF_3)_3(PR_3)_3]$ (PR₃=PPh₃ and PPh₂Me) are described and the trimeric nature has been confirmed in the case of the PPh₃ derivative. The X-ray crystal structure of $[Ag_3(O_3SCF_3)_3(PPh_3)_3]$ shows that each triflate group is in a different coordination mode and that there are two diastereoisomers in the asymmetric unit. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Silver salts have widespread applications in synthetic procedures as halogen abstractors [1,2], one electron oxidants [2-5] or as building blocks [6-14] in the preparation of heteropolynuclear complexes. For all these purposes Ag(OClO₃) has been widely used and some derivatives such as $[Ag(OClO_3)L]$ (L=PPh₃, PPh₂Me or tetrahydrothiophene) have proved to be appropriate synthons for heteronuclear silver complexes. Due to the inherent hazards of metal perchlorates as potential explosives we need to look for similar complexes with other non strong coordinating counterion. The compound $Ag(O_3SCF_3)$ has been used by many authors [15-18] as a safer source of silver ions and we tested $[Ag(O_3SCF_3)L]_n$ as a silver synthon for heteronuclear complexes [19,20]. Here we describe an easier preparation than previously reported for silver triflate derivatives of triphenylthe and methyldiphenyl-phosphine, and also their spectroscopic properties. The X-ray crystal structure of the triphenylphosphine derivative consists of a trinuclear silver complex with the three triflates in three different coordination modes, and the presence of two diastereoisomers in the same unit cells.

2. Experimental

2.1. General procedures

The C, H, S analyses were carried out on a Perkin-Elmer 2400 Microanalyser. Conductivities were measured in approximately 5×10^{-4} mol dm⁻³ acetone solutions, with Jenway 4010 Conductimeter. The melting points were measured using a Gallenkamp apparatus and are uncorrected. The Infrared spectra were recorded (4000–200 cm⁻¹) on a Perkin-Elmer 883 Spectrophotometer, using Nujol mulls between polyethylene sheets. The NMR spectra were recorded on a Bruker ARX 300 Spectrometer, in CD₂Cl₂. Chemical Shifts are cited relative to SiMe₄ (¹H), 85% H₃PO₄ (external ³¹P) and CFCl₃ (¹⁹F). Mass spectra were recorded on VG Autospec LSIMS Technique using 3-nitrobenzylalcohol as a matrix and a Cesium gun.

2.2. Preparation of $[Ag_3(O_3SCF_3)_3(PR_3)_3]$ [L=PPh₃ (1), PPh₂Me (2)]

To a diethyl ether (30 cm³) solution of $[Ag(O_3SCF_3)]$ (0.252g, 1 mmol), was added PPh₃ (0.262 g, 1 mmol) or PPh₂Me (0.200 g, 1 mmol). After 1 h the solution was concentrated in vacuum until 5 cm³ and after addition of hexane (30 cm³) led the precipitation of the new complexes as white solids. Yield%: 85 **1**, 82 **2**. ¹H NMR: **1**: δ =7.6–7.3 (m, 15H, Ph). **2**: δ =7.55–7.35 (m, 10H, Ph);

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1.95 (s,br, 3H, Me). ³¹P-{¹H} NMR 1: δ =14.5 (s) at r.t. and 14.7 (dd, ${}^{2}J_{107AgP}$ 740.6 Hz, ${}^{2}J_{109AgP}$ 855.0 Hz) at -80°C. **2**: $\delta = -1.7$ (s) at r.t. and -1.8 (dd, ${}^{2}J_{107AgP} = 768.0$ Hz, ${}^{2}J_{109AgP} = 875.9$ Hz) at $-80^{\circ}C$. ¹⁹F NMR **1**: $\delta = -78.0$ (s). **2**: $\delta = -77.7$ (s). Mass spectra, m/z(%): 1: 1409(2) $([Ag_{3}(O_{3}SCF_{3})_{2}(PPh_{3})_{3}]^{+}),$ 889(15) $([Ag_2(O_3SCF_3)(PPh_3)_2]^+), 369(100) ([Ag(PPh_3)]^+). 2:$ $([Ag_{3}(O_{3}SCF_{3})_{2}(PPh_{2}Me)_{3}]^{+}),$ 1223(1)765(9) $([Ag_{2}(O_{3}SCF_{3})(PPh_{2}Me)_{2}]^{+}),$ 307(100) $([Ag(PPh_2Me)]^+)$ M.p. 132°C **1**, 78°C (decomp.) **2**. Elemental analysis 1 $C_{57}H_{45}Ag_3F_9O_9P_3S_3$ (1557.63): calcd. C 43.9, H 2.9, S 6.2; found: C, 44.1; H, 3.0; S, 6.5; $2 C_{42}H_{39}Ag_{3}F_{9}O_{9}P_{3}S_{3}$ (1371.47): calcd. C 36.8, H 2.5, S 7.0; found C 36.5, H 2.8, S 7.3. $\Lambda_{\rm M}$ in acetone 1: 122, 2: $124 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$. In dichloromethane **1**: 3.8, **2**: 2.4 $ohm^{-1} cm^2 mol^{-1}$.

2.3. X-ray determination of compound 1

Single crystals were grown by diffusing hexane into a dichloromethane solution of complex (1) at room temperature and mounted in inert oil.

2.4. Crystal data and data collection parameters

C₁₁₄H₉₀Ag₆F₁₈O₁₈P₆S₆, *M*=3115.26, monoclinic, a= 25.896(4), *b*=13.1150(10), *c*=35.578(4)Å, *β*= 106.89(2)°, *U*=11562(2)Å³, T=150K, space group P2₁/n, graphite monochromated Mo-Kα radiation λ=0.71069 Å, *Z*=4, *D*_c=1.790 Mg m⁻³, F(000)=6192, colorless prism with dimensions 0.18×0.16×0.14 mm, μ=1.283 mm⁻¹; Delft Instruments FAST TV area detector diffractometer positioned at the window of a rotating-anode generator, following procedures described elsewhere [21], *θ* range for data collection 1.76 to 25.73°, -28≥h≥0, 0≥h≥18, -14≥ k≥0, 0≥k≥11, -43≥l≥0, 0≥l≥42; 32686 reflections collected, 16224 independent (*R*_{int}=0.1444).

2.5. Structure solution and refinement

The structure was solved by direct methods using SHELXS 86 [22], and refined by full-matrix least squares on F_o^2 , using the program SHELXL 93 [23]. All data used were corrected for Lorentz-polarization factors, and subsequently for absorption using the program DIFABS [24]. The non-hydrogen and non-carbon atoms were refined with anisotropic thermal parameters. All hydrogen atoms were included in idealized positions. The refinement was performed with rigid bond restrictions in some oxygen atoms. Refinement proceeded to R=0.0370, wR=0.0579 for 2339 data with $I_o > 2\sigma$ (I_o) and goodness of fit on F^2 0.356 for 943 parameters and 30 restraints, and R=0.2565, wR=0.1095 for all data. In the final Fourier synthesis the electron density fluctuates in the range 0.387 to -0.481 e Å⁻³. CCDC number 102746.

3. Results and discussion

The addition of the corresponding phosphine to a diethylether solution of $[Ag(O_3SCF_3)]$ in a 1:1 ratio is an easier way to synthesize $[Ag_3(O_3SCF_3)_3(PR_3)_3]$ (PR₃= PPh_3 , 1; PPh_2Me , 2) than previously reported [20]. The spectroscopic data for complexes 1 and 2 are in agreement with the proposed estoichiometry. IR spectra show absorptions at 1285 (vs, br), 1250 (vs, br), 1224 (vs), 1209 (vs) and 1170 (vs, br) for 1 and 1316 (vs), 1288 (vs, br), 1231 (vs), 1223 (vs) and 1184 (vs, br) for 2 which can be assigned to a covalent coordination of the triflate group [25,26]. In accordance with that their dichloromethane solutions behave as non conductors, although the acetone solutions show conductivities characteristic of 1:1 electrolytes, probably because of the replacement of triflate by solvent molecules [19,20,27]. The ${}^{31}P{}^{1}H{}$ NMR spectra at room temperature consist of broad singlets which split into two doublets at -80° C because of the presence of two isotopomers with ${}^{2}J_{107AgP}$ =740.6 Hz, and ${}^{2}J_{109AgP}$ =855.0 Hz in **1** and ${}^{2}J_{107AgP}$ =768.0 Hz, ${}^{2}J_{109AgP}$ =875.9 Hz in **2**. The magnitude of the Ag-P coupling constants have been related with the coordination core for series of nitrate triphenylphosphine silver(I) complexes. So complexes $[Ag(NO_3)(PPh_3)_n]$ show different coupling constants [28,29] that depend on the values of n: n=4 (P₄ coordination core) J_{107AgP} =109 Hz, n=3 (P₃O coordination core) J_{107AgP} =310 Hz and n=2 (P₂O₂ coordination core) J_{107AgP} =470 Hz. Although the latter values belong to c.p.m.a.s values, the data found in CD₂Cl₂ solutions for complexes 1 and 2 point to a coordination core with a high contribution of oxygen atoms which probably requieres a non mononuclear structure. On the other hand, the ¹⁹F NMR spectra show singlets at room temperature which persist even at -80° C. The liquid secondary ion mass spectra (LSIMS+) show the trinuclear ion less a triflate anion $[Ag_3(O_3SCF_3)_2(PR_3)_3]^+$, as well as the corresponding di- $[Ag_2(O_3SCF_3)(PR_3)_2]^+$ and mono-nuclear species $[Ag(PR_3)]^+$, the latter being the base peak in both complexes. The presence of trinuclear species and the absence of higher nuclearities can be considered as evidence of the trinuclear structure of these complexes.

The molecular structure of the complex $[Ag_3(O_3SCF_3)_3(PPh_3)_3]$, has been established by X-ray diffraction and is shown in Fig. 1. Selected bond lengths and angles are given in Table 1. Although the crystal and thus the data were not of good quality, the resolution and refinement of the structure confirms the trimeric nature of 1 and it consists of two trimeric molecules that are conformational isomers of each other. In the first of them, the three silver centers are each bonded to one triphenylphosphine and the triflate units bridge the metal centers. One silver atom, Ag(2), is in a trigonal-planar arrangement, bonded to its one phosphine with an Ag-P distance of 2.363(5)Å and two oxygen atoms from different triflates with Ag-O distances of 2.492(13) and



Fig. 1. Molecule of the complex [Ag₃(O₃SCF₃)₃(PPh₃)₃] in the crystal.

Table 1 Selected bond lengths (Å) and angles (°) for $[Ag_3(O_3SCF_3)_3(PPh_3)_3]$ (1)

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Ag(1)-P(1)	2.327(5)	Ag(1)-O(32)	2.338(14)
Ag(1)-O(21)	2.388(11)	Ag(1)-O(12)	2.546(12)
Ag(2)-O(31)	2.236(12)	Ag(2)-P(2)	2.363(5)
Ag(2)-O(11)	2.492(13)	Ag(3)-O(21)	2.29(2)
Ag(3)-P(3)	2.341(5)	Ag(3)-O(33)	2.432(11)
Ag(3)-O(12)	2.467(10)	S(1)-O(12)	1.449(11)
S(1)-O(13)	1.454(10)	S(1)-O(11)	1.482(14)
S(1)-C(1)	1.78(2)	S(2)-O(23)	1.407(11)
S(2)-O(21)	1.430(13)	S(2)-O(22)	1.440(12)
S(2)-C(2)	1.77(2)	S(3)-O(32)	1.47(2)
S(3)-O(31)	1.472(12)	S(3)-O(33)	1.480(11)
S(3)-C(3)	1.81(2)		
P(1)-Ag(1)-O(32)	117.1(3)	P(1)-Ag(1)-O(21)	134.8(4)
O(32)-Ag(1)-O(21)	94.8(4)	P(1)-Ag(1)-O(12)	134.7(3)
O(32)-Ag(1)-O(12)	89.2(4)	O(21)-Ag(1)-O(12)	71.7(4)
O(31)-Ag(2)-P(2)	157.4(3)	O(231)-Ag(2)-O(11)	97.6(4)
P(2)-Ag(2)-O(11)	104.9(3)	O(21)-Ag(3)-P(3)	144.7(3)
O(21)-Ag(3)-O(33)	94.9(5)	P(3)Ag(3)-O(33)	104.5(3)
O(21)-Ag(3)-O(12)	74.8(4)	P(3)-Ag(3)-O(12)	136.5(3)
O(33)-Ag(3)-O(12)	81.5(4)	O(12)-S(1)-O(13)	115.0(8)
O(12)-S(1)-O(11)	115.4(7)	O(13)-S(1)-O(11)	114.0(8)
O(12)-S(1)-C(1)	106.0(9)	O(13)-S(1)-C(1)	104.4(8)
O(11)-S(1)-C(1)	99.8(10)	S(1)-O(11)-Ag(2)	106.4(6)
S(1)-O(12)-Ag(3)	128.9(7)	S(1)-O(12)-Ag(1)	111.7(5)
Ag(3)-O(12)-Ag(1)	96.1(4)	O(23)-S(2)-O(21)	114.5(10)
O(23)-S(2)-O(22)	118.0(8)	O(21)-S(2)-O(22)	114.5(7)
O(23)-S(2)-C(2)	104.0(9)	O(21)-S(2)-C(2)	99.8(9)
O(22)-S(2)-C(2)	102.6(10)	S(2)-O(21)-Ag(3)	125.9(7)
S(2)-O(21)-Ag(1)	127.3(8)	Ag(3)-O(21)-Ag(1)	105.7(5)
O(32)-S(3)-O(31)	115.8(7)	O(32)-S(3)-O(33)	114.4(8)
O(31)-S(3)-O(33)	116.4(8)	O(32)-S(3)-C(3)	101.3(10)
O(31)-S(3)-C(3)	101.8(9)	O(33)-S(3)-C(3)	104.0(8)
S(3)-O(31)-Ag(2)	129.2(7)	S(3)-O(32)-Ag(1)	133.3(7)
S(3)-O(33)-Ag(3)	138.6(8)		
S(3) - O(33) - Ag(3)	138.0(8)		

2.236(12)Å. The four atoms Ag(2), P(2), O(11) and O(31) belong to the same plane, Ag(2) being 0.021Å out of this plane. The other silver atoms, Ag(1) and Ag(3), are in distorted tetrahedral configurations and are bonded to one phosphine with Ag-P distances of 2.327(5) and 2.341(5)Å both slightly shorter than that mentioned above. All are in the range found for other Ag(PPh₃) fragments [12–14,28–30]. The tetrahedral arrangement is completed by three oxygen atoms, one from each triflate unit with variable Ag-O distances, from 2.29(2)Å (Ag(3)-O(21)) to 2.546(12)Å (Ag(1)-O(12)).

Although some examples of monobi- and tri-dentate coordination of the triflate anion have been reported [19,25,26,31–39] this is one of the rare examples with the three triflate ligands in three different coordination modes. One is monodentate, the one with S(2), so it possesses two free oxygen atoms O(22) and O(23), while the other one, O(21), acts as a bridge between Ag(1) and Ag(3) (μ_2 1:3 κ^2 O). The S(1) triflate unit is bidentate, with the O(13) atom free. O(11) is bonded only to Ag(2) and O(12) is bridging to Ag(1) and Ag(3), so this triflate acts as bridge for the three metal centers ($\mu_3 \ 2\kappa O$, 1:3 $\kappa^2 O'$). The S(3) triflate unit is tridentate, acting like a bridge for all the silver atoms, but each oxygen from this ligand is bonded only to one silver ($\mu_3 \ 1\kappa O, 2\kappa O', 3\kappa O''$). The Ag-O bond length between Ag(2) and the latter triflate unit mentioned, 2.236(12)Å, is the shortest found with this type of ligands. The above mentioned $[\{HgAg_2(mes)_2(O_3SCF_3)_2\}_2]$ [19] has one of its Ag-O distances 2.300(8)Å, being previously the smallest.

These trimers have four optically active atoms, the sulfur from the triflate units, except the monodentate one, and the two tetrahedral silver atoms. In both molecules these centers are in the same configuration, except S(1) (labelled S(4) in the other molecule), that is in a different configuration, see Fig. 2; the molecules are diasteroisomers.

The mass spectra seem to indicate that the trinuclear structure remains in solution as by the high Ag-P coupling constants characteristic of a PO₃ coordination core in the NMR spectra. On the other hand, the presence of only one type of phosphorus, even at -80° C, as well as only one type of trifluoromethyl group indicates that the trinuclear structure either is not the same in solution as in the solid state or the triflate anions are moving in the NMR time scale making both triflate and phosphine units, respectively, equivalent.

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Fig. 2. Schematic view of both molecules, highlighting the different configuration of S(1) and S(4).

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