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# Thermal and spectroscopic studies of Ag(I) complexes with trimethylphosphine and perfluorinated carboxylates

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## Abstract

Silver(I) complexes with trimethylphosphine and perfluorinated carboxylates of the general formula $[Me_3PAgOOCR]_2$, where R = $C_2F_5$, $C_3F_7$, $C_6F_{13}$, $C_7F_{15}$, $C_8F_{17}$, $C_9F_{19}$, $C_6F_5$ and $Me_3PAgOOC(CF_2)_3$ have been prepared and their thermal decomposition studied. Thermal decomposition proceeded in multistages, starting with the detachment of carboxylates and followed by trimethylphosphine dissociation. The final product was metallic silver. The temperatures of silver formation were in the 473–633 K range. Complexes were characterised by $^{13}C$, $^{19}F$, $^{31}P$ NMR and vibrational spectra. Spectral analysis favoured Ag(I) trigonal coordination with unidentate trimethylphosphine and bidentate carboxylates forming bridges between silver(I) ions. © 1997 Elsevier Science B.V.

*Keywords:* Ag(I) complexes; IR and NMR; Perfluorinated carboxylic acids; Thermal analysis; Trimethylphosphine

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## 1. Introduction

Coordination compounds of noble metals are extensively studied for their possible applications as precursors for chemical vapour deposition (CVD) of metals (Ag, Au) or oxides (Cu) [1–5]. Volatility of $Ag^I$, $Au^I$ and $Au^{III}$ complexes with oxygen bonded ligands [6–15] prompted us to study analogous silver(I) complexes. As the oxygen donor ligands which were chosen carboxylates, that are able to bind in uni- or bidentate (chelating or bridging) mode, hence one may expect multinuclear complexes. Many crystal structures of Ag(I) complexes confirmed the presence of the bridging carboxylates [16–19], but in $(Ph_3P)_2Ag(OOCH)$ the formate appeared to be unidentate bonded [20] and a chelating carboxylate was rarely found in a Ag(I) complex [21]. It is also of interest to study the influence of the chain length and the effect of electronegative fluorine atoms on the thermal stability of the Ag–O bond. As found earlier [10], volatility of Ag(I) complexes with $Ph_3P$ and perfluorinated carboxylates was insufficient for CVD purposes, hence trimethylphosphine ($Me_3P$) was chosen to improve the volatility. In addition, trimethylphosphine enhances the stability of Ag–O bond, because Ag(I) is a soft acid which forms unstable bonds with hard O atoms. The main purpose of our studies was analysis of the thermal decomposition processes and spectral characteristics of $[Me_3PAgOOCR]_2$ complexes, where R = $C_2F_5$, $C_3F_7$, $C_6F_{13}$, $C_7F_{15}$, $C_8F_{17}$, $C_9F_{19}$, $C_6F_5$ and $Me_3PAgOOC(CF_2)_3$. The mechanism of thermal

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decomposition is proposed and temperatures of the final product formation is discussed in relation to future CVD applications.

## 2. Experimental

Perfluorinated carboxylic acids (98–99%) and $Me_3P$ (99%, 1 M solution in tetrahydrofuran) were purchased from Aldrich, whereas analytical grade $AgNO_3$ was obtained from POCh Gliwice (Poland).

All reactions were carried out under argon. Solvents were purified and dried by standard methods. Complexes were obtained by the reaction of $[Ag(OOCR)]_2$, where R = $C_2F_5$, $C_3F_7$, $C_6F_{13}$, $C_7F_{15}$, $C_8F_{17}$, $C_9F_{19}$, $C_6F_5$ and $OOC(CF_2)_3$ [22], with $Me_3P$. $Me_3P$ (0.004 mol) in tetrahydrofuran was mixed with a suspension of $[Ag(OOCR)]_2$ (0.002 mol) in ethanol and stirred in the dark until the reaction mixture became clear, which gave colourless crystals after evaporation under vacuum. The complexes Ag(I) thus obtained were recrystallised from dichloromethane. Silver was determined by the argentometric method, after acidification with sulphuric acid. Carbon and hydrogen were determined by elemental semi-microanalysis.

The results of elemental analyses were (% calculated/found):

1. $C_{12}H_{18}F_{10}O_4P_2Ag_2$ – Ag(31.1/31.0), C(20.8/20.6), H(2.6/2.4);
2. $C_{14}H_{18}F_{34}O_4P_2Ag_2$ – Ag(27.2/27.0), C(21.2/20.9) H(2.3/2.1);
3. $C_{20}H_{18}F_{26}O_4P_2Ag_2$ – Ag(19.7/19.5), C(22.0/21.7), H(1.7/1.9);
4. $C_{22}H_{18}F_{30}O_4P_2Ag_2$ – Ag(18.1/18.0), C(22.1/22.2), H(1.5/1.3);
5. $C_{24}H_{18}F_{34}O_4P_2Ag_2$ – Ag(16.7/16.5), C922.3/22.0), H(1.4/1.2);
6. $C_{26}H_{18}F_{38}O_4P_2Ag_2$ – Ag(15.5/15.3), C(22.4/22.0), H(1.3/1.1),
7. $C_{20}H_{18}F_{10}O_4P_2Ag_2$ – Ag(27.3/27.0), C(30.4/30.1), H(2.3/2.2),
8. $C_{11}H_{18}F_6O_4P_2Ag_2$ – Ag(35.6/35.3), C(21.8/21.5), H(3.0/2.8).

IR spectra were obtained with a Bruker JFS 113v FTIR spectrometer using KBr discs, whereas polyethylene discs were used for the range below 400 $cm^{-1}$. Spectra obtained in KBr were compared with the that obtained in Nujol mull with the same data acquisition parameters and they appeared to be identical in the 1700–1000 $cm^{-1}$ range. NMR spectra were recorded on a Varian Gem 200 MHz spectrometer. Samples were dissolved in $CDCl_3$ and DMSO. $^{13}C$ spectra were recorded at 50 MHz, $^{19}F$ at 188 MHz and $^{31}P$ at 81 MHz in 300 K. References used were: tetramethylsilane for $^{13}C$; $CCl_3F$ for $^{19}F$; and 85% $H_3PO_4$ for $^{31}P$. Solvent for $^{31}P$ NMR was $CDCl_3$, at a temperature of 300 K and concentration of $1 \times 10^{-3}$ M.

Thermal studies were performed on a MOM OD-102 Derivatograph (Paulik and Paulik, Hungary). Samples (50 mg) were run under nitrogen, heated up to 773 K, at a rate of 3.5 K $min^{-1}$, TG sensitivity – 50 mg, the reference material – $Al_2O_3$.

Powder X-ray diffraction data were obtained with a Dron 1 (USSR) diffractometer using $CuK_\alpha$ radiation.

## 3. Results and discussion

### 3.1. Thermal analysis

Results of the thermal analysis performed in nitrogen are listed in Table 1. Decomposition processes started in the 323–428 K range and exhibit one exothermic transition in the DTA, except complex $[Me_3PAgOOCC_6F_5]_2$ (7) for which the first stage was endothermic and the second exothermic (Fig. 1). The endothermic transition found for complex (7) can be related to electron acceptor properties of the pentafluorobenzoic residue. The exotherms correspond to the mass loss in the TG curves which can be correlated with quantitative detachment of carboxylate and trimethylphosphine (Table 1). However, the DTG curve analysis revealed that both molecules dissociate in two successive processes. Because the onset of the second reaction overlaps with the completion of the first, these processes were not resolved in the DTA curves; only the DTG curves indicate it. A similar decomposition mechanism was observed for Au(I) and Ag(I) complexes with the identical carboxylates and triphenylphosphine [23,24] or triethylphosphine ($Et_3P$) [25,26]. The observed onset temperatures of the first exotherm can be taken as the measured Ag–O bond strength

Table 1
Results of thermal analysis

| Complex | Heat | Temperature [K] | | | Weight loss (%) | | Detached |
|---|---|---|---|---|---|---|---|
| | effect | $T_i$ [a] | $T_m$ [b] | $T_f$ [c] | found | calculated | groups |
| (1) $[Me_3PAgOOCC_2F_5]_2$ | exo | 428 | 473 | 513 | 68.5 | 68.9 | $C_3F_5O_2 + Me_3P$ |
| (2) $[Me_3PAgOOCC_3F_7]_2$ | exo | 383 | 473 | 493 | 72.5 | 72.8 | $C_4F_7O_2 + Me_3P$ |
| (3) $[Me_3PAgOOCC_6F_{13}]_2$ | exo | 413 | 463 | 503 | 83.0 | 83.3 | $C_7F_{13}O_2 + Me_3P$ |
| (4) $[Me_3PAgOOCC_7F_{15}]_2$ | exo | 403 | 463 | 483 | 81.5 | 81.9 | $C_8F_{15}O_2 + Me_3P$ |
| (5) $[Me_3PAgOOCC_8F_{17}]_2$ | exo | 403 | 453 | 473 | 83.0 | 83.3 | $C_9F_{17}O_2 + Me_3P$ |
| (6) $[Me_3PAgOOCC_9F_{19}]_2$ | exo | 393 | 463 | 508 | 86.0 | 86.3 | $C_{10}F_{19}O_2 + Me_3P$ |
| (7) $[Me_3PAgOOCC_6F_5]_2$ | endo | 323 | 343 | 348 | 15.5 | | |
| | exo | 353 | 451 | 463 | 52.0 | 67.9 | |
| | — | 468 | — | 593 | 5.0 | 4.8 | $C_6F_5O_2 + Me_3P$ |
| (8) $Me_3PAgOOC(CF_2)_3COOAgPMe_3$ | exo | 408 | 433 | — | | | |
| | exo | — | 453 | 633 | 64.0 | 64.4 | $C_5F_6O_4 + 2Me_3P$ |

[a] Initial temperature.
[b] Maximum temperature.
[c] Final temperature.

[23]. The lowest onset temperature in the examined series of complexes was found for $[Me_3PAgOOCC_6F_5]_2$. The observed changes in the stability of Ag–O bond can be related to the stronger $\pi$-electron acceptor character of the pentafluorophenyl ring than to the perfluorinated aliphatic chains. As a result, Ag(I) becomes a harder acid than in the other complexes and the thermal stability of Ag–O bond has decreased. The Ag–O bond strength is also affected by $Me_3P$, as the onset temperatures are significantly lower in comparison to $Ph_3P$ and $Et_3P$ complexes (ca. 60 K and 45 K, respectively) [23,25]. This can be explained by the weaker $\sigma$-donor properties of $Me_3P$, in relation to $Et_3P$ and $Ph_3P$. The highest onset temperature of the decarboxylation process was found for $[Me_3PAgOOCC_2F_5]_2$ (428 K), which is ca. 5 K lower than for the analogous complex with $Et_3P$. The slight increase can be caused by the short perfluorinated chain which diminishes the polarization of Ag–O bond and enhances its stability. The Ag–O bond thermal stability for the complexes having the general formula $[R_3PAgOOCR]_2$ (where R′ – perfluorinated chain or ring, and R′ – $CH_3$, $C_2H_5$, $C_6H_5$) changes in the following sequence $Me_3P < Et_3P < Ph_3P$, which is typical for the copper triad metal complexes [23,26].

The second step of the decomposition corresponds to the detachment of $Me_3P$. The dissociation of $Me_3P$ coincides with decarboxylation which prevents determination of the onset temperatures of the second stage. The final product of the decomposition reaction is metallic silver, which is evident from the analysis of powder X-ray diffraction and the TG curve calculations. The yield of silver is quantitative, and suggests the lack of complex sublimation under experimental conditions. The silver(I) salts with the same perfluorinated carboxylates also decomposed to silver [22]. Nonfluorinated Ag(I) carboxylates decompose to silver in exothermic processes [27–29], but for perfluorinated the two-stage process (endo- followed by exotherm) without clearly separated decarboxylation from dealkylation was found. The lowest temperature of silver formation was in the case of $[C_6F_5COOAg]_2$ (553 K). For the complexes, this feature was found for $[Me_3PAgOOCC_6F_5]_2$ (348 K), which makes this complex a promising precursor for CVD purposes. A surprisingly high temperature of silver formation was found for $[Me_3PAgOOCC_2F_5]_2$ (513 K), but it is still below the limit for CVD purposes (max. 620 K) and the lowest temperature for $[RCOOAg]_2$. Temperatures of silver formation for the complexes are ca. 150 K lower than for the respective Ag(I) complexes with $Ph_3P$ and 15 K lower in relation to $Et_3P$ complexes [23,25]. The same trend was observed for Au(I) complexes with the similar ligands [24,26].

### 3.2. NMR spectra analysis

The chemical shifts for $^{13}C$, $^{19}F$, $^{31}P$ resonances of the complexes are listed in Table 2. $^{31}P$ resonance appeared in the −35.4-to-36.8 ppm range, which is

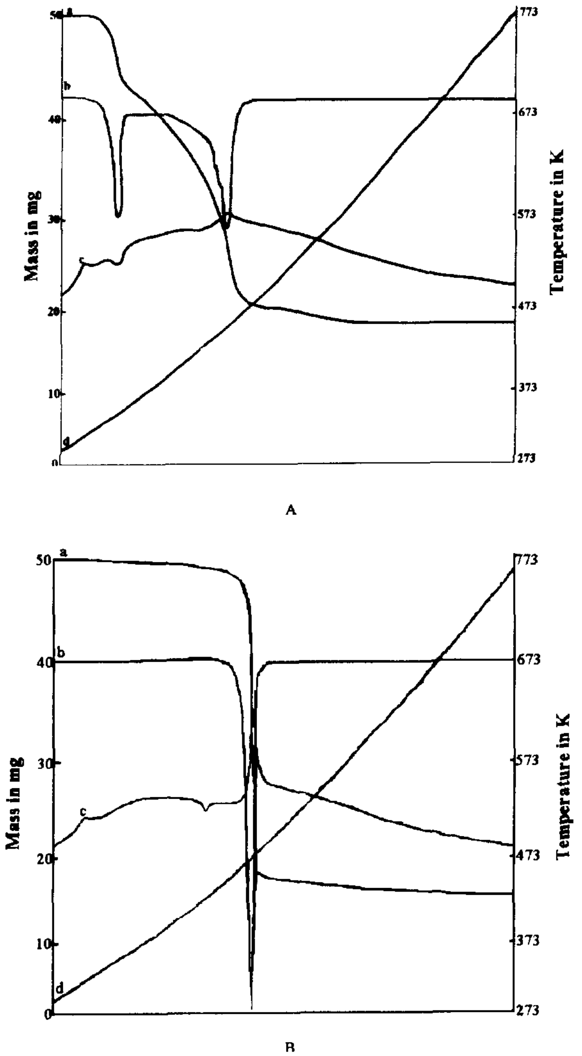

Fig. 1. Thermal decomposition of Ag(I) complexes. (A) – $[Me_3PAgOOCC_6F_5]_2$. (B) – $[Me_3PAgOOCC_3F_7]_2$: (a) TG-; (b) DTG-; (c) DTA- and (d) T-curves.

23.5–24.9 ppm downfield in relation to $Me_3P$ (Table 2), thus suggesting coordination of the $Me_3P$ molecule. $^{13}C$ resonance of the COO carbon upon coordination revealed the most significant changes. Spectra of the complexes exhibit COO resonances shifted downfield (except complex 1) 1.0–2.7 ppm in relation to the free acids. Downfield coordination shift can be explained by the lower negative charge on the carbon in the COO group caused by Ag–O bond formation. There is no significant relation between the COO chemical shift and the number of $CF_2$ groups in the aliphatic chain. The fluorine resonances are also affected by the Ag–O bond formation and the most noticeable changes were observed for the $C(2)F_2$ signals (Table 2). The resonance lines of the $CF_2$ groups are shifted upfield upon coordination (0.1–3.3 ppm) in comparison to the free acids. This effect demonstrates the induction shift of the electron charge from the Ag–O bond to the electronegative fluorine.

### 3.3. *IR spectra analysis*

Carboxylates can coordinate to metal ions in a number of ways, such as unidentate, chelating or bridging [30,31]. The reported correlations between the mode of carboxylate linkage and C–O bond stretching frequencies were used in the presented studies for determination of the Ag(I) coordination number and symmetry of the coordination sphere [32]. An analysis of COO group frequencies gives a $\Delta_{COO} = \nu_{as} - \nu_s$ (as – asymmetric, s – symmetric) value, which is then compared with that for the sodium salts. The calculated $\Delta_{COO}$ values for the studied complexes are in the range characteristic for carboxylates bridging two Ag(I) ions (Table 3). Nakamoto [31] suggested this type of linkage in the case when the $\Delta$ values for the sodium salts and the complexes are similar. This can be explained by comparable C–O distances in ionic and bridging carboxylates which results in almost identical $\nu_{as}$ and $\nu_s$ frequencies. Bridging carboxylates were found in Ag(I) complexes with carboxylates and $Ph_3P$ [23,33], and in silver(I) carboxylates [16,17].

The absorption bands of trimethylphosphine confirm the coordination, however P–C stretching vibration bands are shifted only ca. 10 cm$^{-1}$ to higher frequencies, in comparison to the spectrum of free $Me_3P$ [34,35]. The Ag–P stretching vibration bands appeared in the 223–239 cm$^{-1}$ range, which is consistent with the reported frequencies [36]. The Ag–O asymmetric stretching vibrations bands emerged in the 328–339 cm$^{-1}$ range, whereas the symmetric band was found at 190–198 cm$^{-1}$ (in the spectra of 1, 3, 4, 7, 8) [37]. Two absorption bands of Ag–O (asymmetric and symmetric) are in favour of $C_{2v}$ microsymmetry of the coordination sphere. The IR spectra analysis and the results of NMR spectra suggest

Table 2
$^{13}C$, $^{19}F$, $^{31}P$ NMR spectral analysis [ppm]

| Complex | $^{13}C$ | | $^{19}F$ | | $^{31}P$ | |
|---|---|---|---|---|---|---|
| | $\delta$ COO | $\Delta_1$ [c] | $\delta$ C(2)$F_2$ | $\Delta_2$ [d] | $\delta$ | $\Delta_3$ [e] |
| (1) $[Me_3PAgOOCC_2F_5]_2$ | 162.5 | −0.8 | −41.8 | 3.1 | −36.3 | 24.0 |
| (2) $[Me_3PAgOOCC_3F_7]_2$ | 163.2 | 1.0 | −49.6 | 0.1 | −35.4 | 24.9 |
| (3) $[Me_3PAgOOCC_6F_{13}]_2$ [a] | 163.0 | 2.3 | −38.4 | 3.3 | −35.7 | 24.6 |
| (4) $[Me_3PAgOOCC_7F_{15}]_2$ [a] | 163.1 | 2.6 | −38.5 | 3.0 | −36.3 | 24.0 |
| (5) $[Me_3PAgOOCC_8F_{17}]_2$ [a] | 162.5 | 2.3 | −38.6 | 3.0 | −36.3 | 24.0 |
| (6) $[Me_3PAgOOCC_9F_{19}]_2$ [a] | 162.8 | 2.7 | −38.6 | 2.9 | −36.2 | 24.1 |
| (7) $[Me_3PAgOOCC_6F_5]_2$ [b] | 161.8 | 2.5 | — | — | −36.8 | 23.5 |
| (8) $Me_3PAgOOC(CF_2)_3COOAgPMe_3$ | 163.0 | — | −38.4 | — | −36.3 | 24.0 |

[a] $^{13}C$ spectra recorded in DMSO.
[b] $\delta$ CF (complex): $m$ – 84.5 ($\Delta m = 2.0$); $o$ – 63.8 ($\Delta o = -5.0$); p – 77.2 ($\Delta p = -8.5$).$\Delta m = \delta m$CF(complex) – $m$CF(acid); $\Delta o = \delta o$CF(complex) – $o$CF(acid); $\Delta p = \delta p$CF(complex) – CF(acid);m = meta, $o$ = *orto*, $p$ = *para*.
[c] $\Delta_1 = \delta$COO(complex) – $\delta$COO(acid)
[d] $\Delta_2 = \delta C(2)F_2$(complex) – $\delta C(2)F_2$(acid).
[e] $\Delta_3 = \delta$(complex) – $\delta(Me_3P)$; $\delta(Me_3P) = -60.3$ ppm.

Table 3
Characteristic absorption bands in IR spectra ($cm^{-1}$)

| Complex | $\nu_{as}$COO | $\nu_s$COO | $\Delta_1$ [a] | $\Delta_2$ [b] | $\nu$Ag–P | $\nu$Ag–O |
|---|---|---|---|---|---|---|
| (1) $[Me_3PAgOOCC_2F_5]_2$ | 1670 | 1405 | 265 | 268 | 226 | 339<br>196 |
| (2) $[Me_3PAgOOCC_3F_7]_2$ | 1686 | 1405 | 281 | 272 | 223 | 338 |
| (3) $[Me_3PAgOOCC_6F_{13}]_2$ | 1684 | 1397 | 287 | 272 | 235 | 330<br>190 |
| (4) $[Me_3PAgOOCC_7F_{15}]_2$ | 1680 | 1412 | 268 | 272 | 226 | 336<br>198 |
| (5) $[Me_3PAgOOCC_8F_{17}]_2$ | 1662 | 1405 | 257 | 272 | 231 | 334 |
| (6) $[Me_3PAgOOCC_9F_{19}]_2$ | 1662 | 1408 | 254 | 276 | 226 | 328 |
| (7) $[Me_3PAgOOCC_6F_5]_2$ | 1663 | 1416 | 247 | 201 | 239 | 338<br>198 |
| (8) $Me_3PAgOOC(CF_2)_3COOAgPMe_3$ | 1668 | 1410 | 258 | — | 235 | 329<br>193 |

[a] $\nu_{as}$COO-$\nu_s$COO (in complex).
[b] $\nu_{as}$COO-$\nu_s$COO (in sodium salt).

trigonal Ag(I) coordination with bridging perfluorinated carboxylates and unidentate $Me_3P$. The length of the aliphatic chain and the number of fluorine atoms have no influence on the carboxylate coordination mode.

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