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Thermal studies of Ag(I) complexes with triethylphosphine and perfluorinated carboxylates

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Abstract

Silver(I) complexes with triethylphosphine and perfluorinated carboxylic acids residues of general formula $[Et_3PAgOOCR]_2$, where R=C_2F_5, C_3F_7, C_6F_{13}, C_7F_{15}, C_8F_{17}, C_9F_{19}, C_6F_5 and $Et_3PAgOOC(CF_2)_3COOAgPEt_3$, were synthesized. Thermal decomposition proceeded in two stages – both exothermic processes corresponding to the elimination of carboxylate and triethylphosphine residues. The final product of the thermal decomposition was metallic silver. Analyses by ^{13}C, ^{19}F, ^{31}P NMR spectroscopy and vibrational spectra suggest trigonal coordination of Ag(I), the coordination sphere consisting of unidentate triethylphosphine and bidentate carboxylates forming bridges between metal ions. © 1998 Elsevier Science B.V.

Keywords: Ag(I) complexes; IR and NMR; perfluorinated carboxylic acids; thermal analysis; triethylphosphine

1. Introduction

Coordination compounds of the copper triad metals have been extensively studied because of their possible applications as precursors in the Chemical Vapour Deposition (CVD) of metal (Au, Ag) or oxide layers (Cu). The volatility of Ag(I) and Au(I) complexes with oxygen bonded ligands (β-diketonates) [1–8] prompted us to study analogous silver(I) complexes with the same donor atoms and triethylphosphine (Et_3P). Carboxylates have been chosen as oxygen donor ligands which are able to bind a uni- or bidentate (chelating or bridging) mode, hence one may expect multinuclear complexes [9–14]. Crystal structures of Ag(I) complexes confirmed the presence of the bridging carboxylates [15–19], but in $(Ph_3P)_2Ag(OOCH)$ the formate appeared to be unidentate bonded [20] and a rare chelating carboxylate was also found [21]. It was also interesting to study the influence of the chain length and the electronegativity of the fluorine atoms on the thermal stability of the Ag–O bond. As found earlier [22], the volatility of Ag(I) complexes with Ph_3P and perfluorinated carboxylates is insufficient for CVD purposes, therefore, triethylphosphine (Et_3P) was chosen. The main goals of our studies were the analysis of the thermal decomposition processes, elucidation of decomposition reactions mechanism and spectral characteristics of $[Et_3PAgOOCR]_2$ 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 $Et_3PAgOOC(CF_2)_3COOAgEt_3$. The temperatures of the final product formation will be discussed in relation to a composition of complexes.

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2. Experimental

Perfluorinated carboxylic acids (98–99%) and Et_3P (99%, 1M solution in tetrahydrofuran) were purchased from Aldrich and $AgNO_3$ analytical grade from POCh Gliwice (Poland). All reactions were carried out under argon. Solvents were purified and dried by standard methods. Complexes were synthesized by reacting $[RCOOAg]_2$ [23], where R=C_2F_5, C_3F_7, C_6F_{13}, C_7F_{15}, C_8F_{17}, C_9F_{19}, C_6F_5 and $AgOOC(CF_2)_3COOAg$ with Et_3P. Et_3P (0.004 mol) in tetrahydrofuran was mixed with ethanol solution, or suspension in the case of the chain above C_6F_{13}, of $[RCOOAg]_2$ (0.002 mol). The reaction was stirred in the dark until a clear solution was formed, which after evaporation on vacuum line gave a colourless oil. Silver was determined argentometrically, after previous complex mineralization. C and H were determined by elemental semi-microanalysis. The results of elemental analyses were as follows (% calc/found):

$$C_{18}H_{30}F_{10}O_4P_2Ag_2,\ Ag(27.7/27.6),\ C(27.8/27.7), H(3.9/3.5); \quad (1)$$

$$C_{20}H_{30}F_{34}O_4P_2Ag_2,\ Ag(24.6/24.4),\ C(27.4/27.4)H(3.5/3.4); \quad (2)$$

$$C_{26}H_{30}F_{26}O_4P_2Ag_2, Ag(18.3/18.0),\ C(26.5/26.2), H(2.6/2.4); \quad (3)$$

$$C_{28}H_{30}F_{30}O_4P_2Ag_2, Ag(16.9/16.6),\ C(26.3/26.0), H(2.4/2.0); \quad (4)$$

$$C_{30}H_{30}F_{34}O_4P_2Ag_2, Ag(25.7/25.4),\ C(26.1/26.0), H(2.2/2.0); \quad (5)$$

$$C_{32}H_{30}F_{38}O_4P_2Ag_2, Ag14.6/14.4),\ C(26.0/25.9), H(2.1/1.9); \quad (6)$$

$$C_{26}H_{30}F_{10}O_4P_2Ag_2, Ag(24.7/24.4),\ C(35.7/35.2), H(3.5/3.0); \quad (7)$$

$$C_{17}H_{30}F_6O_4P_2Ag_2,\ Ag(31.3/31.0),\ C(29.6/29.2), H(4.4/4.0). \quad (8)$$

Thermal analysis was carried out on a MOM OD-102 Derivatograph, Paulik and Paulik (Hungary). The atmosphere over the sample was nitrogen, heating range was up to 773 K, the heating rate 2.5 K/min^{-1}, mass of sample 50 mg (except $[Et_3PAgOOCC_8F_{17}]_2$, where mass of sample was 80 mg); the reference material was Al_2O_3.

The IR spectra were obtained using a Perkin–Elmer 2000 FTIR spectrometer in KBr discs, over the 400–4000 cm^{-1} range. Below 400 cm^{-1} polyethylene discs were used. Spectra obtained in KBr were compared with the same obtained in nujol mull with the same data acquisition parameters and they appeared to be identical in the 1000–1700 cm^{-1} range. NMR spectra were recorded on a Varian Gem 200 MHz spectrometer. Samples were dissolved in $CDCl_3$. ^{13}C spectra were recorded at 50 MHz, ^{19}F at 188 MHz and ^{31}P at 81 MHz. Reference were tetramethylsilane for ^{13}C, CCl_3F for ^{19}F and 85% H_3PO_4 for ^{31}P. ^{31}P NMR spectra in $CDCl_3$ were run at temperature 300 K and concentration 1×10^{-3} M.

Powder X-ray diffraction data were obtained on a Dron 1 (USSR) diffractometer using CuK_α, λ=0.1524 nm.

3. Results and discussion

3.1. Thermal analysis

The results of the thermal analysis performed in nitrogen are listed in Table 1. Decomposition processes started in the 383–423 K range as an exotherm followed by another one (Fig. 1). The exotherms are connected with the mass loss on TG curve which corresponds to exclusion of carboxylate and triethylphosphine residues in two overlapping stages. However, from DTG curve analysis it is evident that both dissociate in two subsequent processes. Because the onset of the second reaction coincide with the final temperature of the first one, we were unable to find the initial temperature of the second stage of decomposition reaction. The similar phenomenon was observed for Ag(I) salts with nonfluorinated carboxylates [24–26] and Ag(I) complexes with the identical carboxylates and triphenylphosphine [22] or trimethylphosphine [27]. The onset temperatures of the first exotherm can be taken as a measure of the Ag–O strength in $[R_3PMOOCR']_2$ type complexes [22]. The lowest onset temperature, observed for $[Et_3PAgOOCC_6F_9]_2$ is 15 K higher than for the analogous complex with Ph_3P [22]. The low stability of Ag–O bond can be explained by the stronger π

Table 1
Results of thermal analysis

	Complex	Heat effect	Temperature (K)			Weight loss (in %)		Detached
			T_i [a]	T_m [b]	T_f [c]	calc.	found	groups
1	$[Et_3PAgOOCC_2F_5]_2$	Exo	423	478	528	72.3	71.9	$C_3F_5O_2+Et_3P$
2	$[Et_3PAgOOCC_3F_7]_2$	Exo	403	458	501	75.4	75.0	$C_4F_6O_2+Et_3P$
3	$[Et_3PAgOOCC_6F_{13}]_2$	Exo	413	453	493	79.6	79.4	$C_6F_{13}O_2+Et_3P$
4	$[Et_3PAgOOCC_7F_{15}]_2$	Exo	418	473	553	83.1	83.0	$C_8F_{15}O_2+Et_3P$
5	$[Et_3PAgOOCC_8F_{17}]_2$	Exo	413	453	523	80.9	81.2	$C_8F_{17}O_2+Et_3P$
6	$[Et_3PAgOOCC_9F_{19}]_2$	Exo	388	458	513	85.4	85.2	$C_{10}F_{19}O_2+Et_3P$
7	$[Et_3PAgOOCC_6F_5]_2$	Exo	383	463	506	75.3	74.8	$C_7F_4O_2+Et_3$
8	$Et_3PAgOOC(CF_2)_3COOAgPEt_3$	Exo	403	458	683	68.8	69.0	$C_5F_6O_4+2Et_3P$

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

electron acceptor character of the pentafluorophenyl ring compared with the perfluorinated aliphatic chain. The Ag–O bond became less covalent than in other complexes and the thermal stability of Ag–O bond decreased. The highest onset temperature (423 K) of the decarboxylation process has been found for $[Et_3PAgOOCC_2F_5]_2$. Most probably, this is an effect of σ electron donor properties of triethylphosphine, and short perfluorinated chain that causes the lower polarization of Ag–O bond and enhances its stability. The complexes with the short aliphatic chain (C_2, C_3) revealed lower onset temperatures of the first step than the analogous Ag(I) complexes with Ph_3P [22]. The weaker stabilization of Ag–O bond in the presence of Et_3P, than Ph_3P, can be related to the σ electron donor properties of triethylphoshine. The decrease of M–O bond stability was also found for copper triad complexes with the analogous ligands [22,27]. The results of thermal analysis conclude that stabilisation of Ag–O bond is influenced by the electron donor acceptor properties of tertiary phosphines. The steric factor has less profound impact because strong π electron acceptor ligand (triphenylphosphine), despite steric hindrances, stabilises Ag–O bond more effectively than less bulky and weak π electron acceptor, such as triethylphosphine. Thermal decomposition of Eq. (8) proceeds in a similar way as the majority of the discussed complexes. Decomposition of initial temperature (403 K) is identical to the heptafluorobutyrate complex. This feature can be related to the same amount of carbon atoms in the aliphatic chain and the fact that both complexes are dimeric. The total mass loss corresponds to the dissociation of carboxylate and 2 mol of triethylphosphine.

The second step of decomposition reaction corresponds to the detachment of Et_3P. The dissociation of Et_3P proceeds immediately after decarboxylation that enables the determination of onset temperatures (Fig. 1). The final product of the decomposition processes is metallic silver, which is evident from the analysis of TG curves and the final product powder diffractograms examination. Observed lines for metallic silver (0.2352, 0.2026, 0.1179, 0.1444, 0.1233 nm) correspond to those reported in Powder Diffraction File [28]. The lowest temperature of silver formation (493 K) was found for $[Et_3PAgOOCC_6F_{13}]_2$, that makes this complex promising precursor for CVD purposes. The surprisingly high temperature of silver formation (553 K) was found for $[Et_3PAgOOCC_7F_{15}]_2$, but still it is in the range acceptable for CVD purposes (max. 620 K). The highest temperature of metal formation (683 K) was detected for Eq. (8) which is out of the range acceptable for CVD precursors. The temperatures of the final product formation for remaining complexes, Eqs. (1)–(7), are lower (in 493–523 K range). Temperatures of silver formation in the studied complexes are ca. 150 K lower than for the respective Ag(I) complexes with identical perfluorinated acids and Ph_3P [22]. The presented series of complexes decomposed in a way characteristic for silver(I) carboxylates and copper triad complexes with tertiary phosphines. Silver(I) salts with aliphatic and aromatic carboxylates also

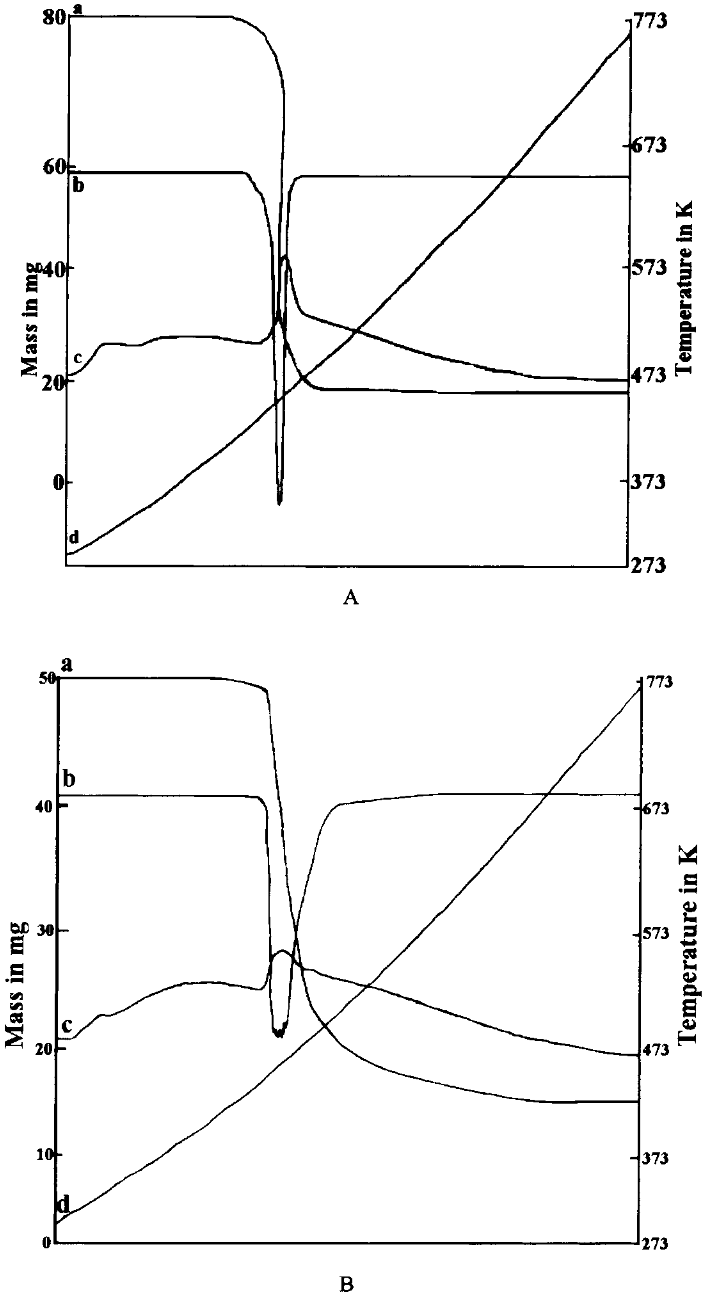

Fig. 1. Thermal decomposition of Ag(I) complexes: (A) $[Et_3PAgOOCC_8F_{17}]_2$ (mass of sample was 80 mg); (B) $Et_3PAgOOC(CF_2)_3COOAg\text{-}PEt_3$; (a) TG-, (b) DTG-, (c) DTA- (d) T-curves.

decomposed to metallic silver in a two-step process (endo- followed by exotherm) and decarboxylation was not exactly separated from dealkylation. Perfluorinated carboxylates, in relation to nonfluorinated one, do not change the decomposition mechanisms but diminish the stability of Ag–O. The lowest stabilisation of the Ag–O bond was found for the perfluorinated aromatic carboxylates whereas the highest for the one with the short perfluorinated chain. This effect suggests that in Ag(I) complexes with carboxylates the electron accepting substituents would stabilise the coordination sphere. The Ag–O bond stability also depends on the electronic properties of tertiary phosphines rather than steric factors and changes in the following sequence: $Me_3P<Et_3P<Ph_3P$. Silver formation temperatures found for the studied complexes (below 620 K) are sufficient for application to the compounds in CVD as silver precursors.

3.2. NMR spectral studies

Chemical shifts for the ^{13}C, ^{19}F, ^{31}P resonances of complexes are listed in Table 2. Single ^{31}P resonance band appeared in the 9.5–13.4 ppm range, i.e. 27.6–31.6 ppm upfield in relation to free Et_3P [29]. The ^{13}C resonances of COO group revealed the most indicative changes imposed by coordination to Ag(I). The signals are shifted downfield 0.6–2.7 ppm in comparison to RCOOH (except Eqs. (1) and (8)) but it is difficult

Table 2
^{13}C, ^{19}F, ^{31}P NMR spectra analysis (in ppm)

	Complex	^{13}C		^{19}F		^{31}P	
		δCOO	Δ_1 [a]	$C(2)F_2$	Δ_2 [b]	δ	Δ_3 [c]
1	$[Et_3PAgOOCC_2F_5]_2$	162.5	−0.8	−41.5	3.4	13.1	31.2
2	$[Et_3PAgOOCC_3F_7]_2$	163.1	0.9	−49.3	0.3	13.0	31.1
3	$[Et_3PAgOOCC_6F_{13}]_2$	161.3	0.6	−38.7	3.0	13.4	31.5
4	$[Et_3PAgOOCC_7F_{15}]_2$	163.0	2.5	−38.2	3.3	13.0	31.1
5	$[Et_3PAgOOCC_8F_{17}]_2$	162.9	2.7	−38.6	3.0	13.3	31.4
6	$[Et_3PAgOOCC_9F_{19}]_2$	161.3	1.2	−39.3	2.2	13.5	31.6
7	$[Et_3PAgOOCC_6F_5]_2$	163.4	−0.9	— [d]	— [d]	12.4	30.5
8	$Et_3PAgOOC(CF_2)_3COOAgPEt_3$	163.8	—	−38.0	—	9.5	27.6

[a] δCOO(complex)−δCOO(acid)
[b] $\delta C(2)F_2$ (complex)−$\delta C(2)F_2$ (acid)
[c] δ(complex)−$\delta(Et_3P)$; $\delta(Et_3P)=-18.1$ ppm
[d] δCF (complex): *m*: −84.5 ($\delta m=-2.0$); *o*: −63.1 ($\delta o=-4.3$); *p*: −77.4 ($\delta p=-8.7$)
$\delta m=\delta m$ CF(complex)$-\delta m$ CF(acid); $\delta o=\delta o$ CF(complex)$-\delta o$ CF(acid); $\delta p=\delta p$ CF(complex)$-\delta p$ CF(acid); *m*=meta, *o*=ortho, *p*=para

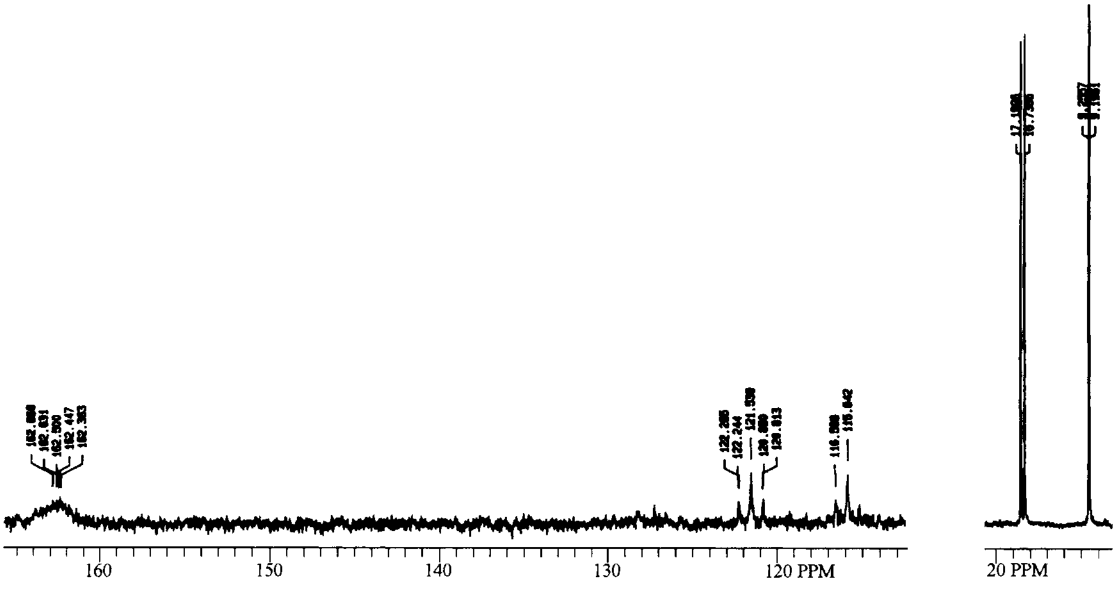

Fig. 2. ^{13}C NMR spectrum of $[Et_3PAgOOCC_2F_5]_2$.

to relate these values with the way of COO coordination (Fig. 2). Downfield shift can be explained by the lower negative charge on carbon in COO group caused by the presence of electronegative fluorine atoms. ^{19}F NMR (Fig. 3) has been also affected by the Ag–O bond formation but the changes were observed only for the signals of $C(2)F_2$ group (Table 2), which upon coordination are shifted downfield (0.3–3.4 ppm) in relation to free acids. The NMR results gave evidences of Et_3P and carboxylates binding to the central ion, but it is difficult to correlate the direction and the magnitude of ^{13}C, and ^{19}F chemical shifts with the way of coordination.

3.3. IR spectral analysis

Carboxylates can coordinate to metal ions in a number of ways, such as uni- or bidentate (chelating or bridging) [30–32], that can be concluded from the IR spectra analyses. For this purpose, correlations

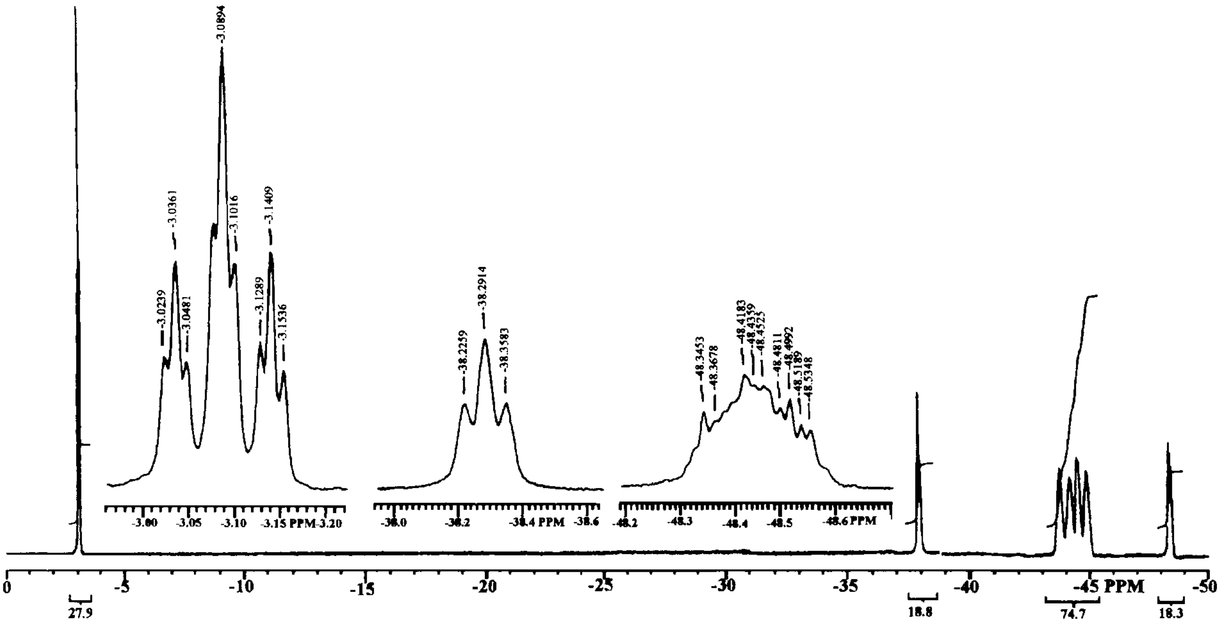

Fig. 3. ^{19}F NMR spectrum of $[Et_3PAgOOCC_7F_{15}]_2$.

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

	Complex	$\nu_{as}COO$	ν_sCOO	Δ_1 [a]	Δ_2 [b]	$\nu Ag–P$	$\nu Ag–O$
1	$[Et_3PAgOOCC_2F_5]_2$	1667	1416	252	268	225	326
2	$[Et_3PAgOOCC_3F_7]_2$	1683	1399	284	272	224	322
3	$[Et_3PAgOOCC_6F_{13}]_2$	1688	1397	291	272	225	333 198
4	$[Et_3PAgOOCC_7F_{15}]_2$	1681	1406	275	272	218	317
5	$[Et_3PAgOOCC_8F_{17}]_2$	1681	1407	254	272	216	327
6	$[Et_3PAgOOCC_9F_{19}]_2$	1662	1406	256	276	222	330
7	$[Et_3PAgOOCC_6F_5]_2$	1656	1396	260	201	217	316
8	$Et_3PAgOOC(CF_2)_3COOAgPEt_3$	1669	1412	257	—	220	326

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

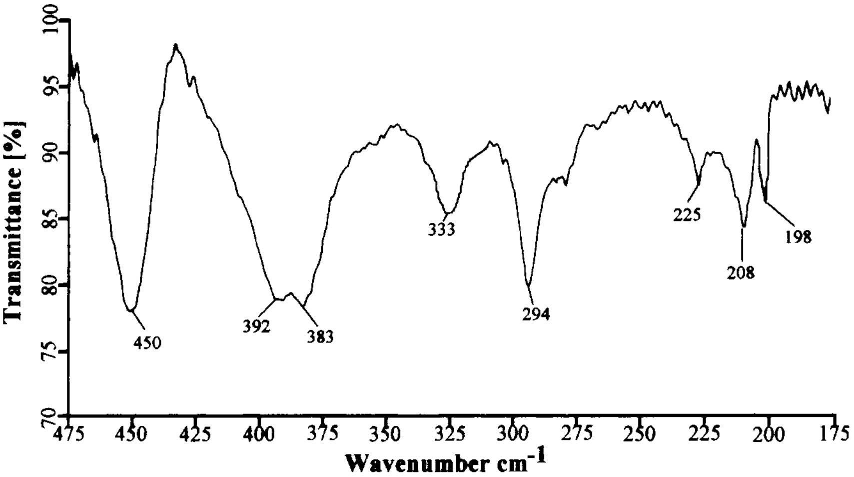

Fig. 4. IR spectrum of $[Et_3PAgOOCC_6F_{13}]_2$ in the range 475–175 cm^{-1}.

between the mode of carboxylate linkage and COO group stretching frequencies have been applied. The calculated (as – asymmetric, s – symmetric) parameter for the complexes is in favour of bridging carboxylates [30,31] (Table 3). Bridging COO groups were found in $[Ph_3PAgOOCC_2F_5]_2$, whose X-ray structure has been reported [33]. Absorption bands of triethylphosphine confirm the coordination, however P–C stretching vibration bands are shifted, in comparison to the spectrum of free Et_3P, less than 10 cm^{-1} [34]. The Ag–O asymmetric stretching vibration bands appeared in the 316–333 cm^{-1} range, (Fig. 4) whereas symmetric band was found at 198 cm^{-1} only in the spectra of Eq. (3)[35]. Ag–P stretching vibration bands appeared in the 216–225 cm^{-1} (Fig. 4) range which is similar to the reported frequencies [36]. Presented results of the NMR and IR spectra examination are in favour of Ag(I) trigonal coordination. Studied complexes appeared to be a dimers and coordination sphere most probably consist of triethylphosphine and carboxylates forming bridges between two silver ions.

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