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Synthesis and crystal structure of silver(I) carboxylate complexes, $Ag(P^nBu_3)[C(CH_3)_3COO]$ and $Ag(Phen)_2[CF_3COO]\cdot H_2O$

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Abstract

$Ag(P^nBu_3)[C(CH_3)_3COO]$ (**I**) and $Ag(Phen)_2[CF_3COO]\cdot H_2O$ (**II**) were synthesized by the reaction of silver (I) carboxylate with the neutral ligand in absolute ether and ethanol, respectively. Crystal structures of **I** and **II** were determined by single crystal X-ray diffraction. The crystal structure of **I** is built up from dimeric units in which two $Ag(P^nBu_3)[C(CH_3)_3COO]$ molecules are linked by two Ag–O bonds (2.626 Å). The closest coordination environment of the silver atom consists of two oxygen atoms with average Ag–O distances of 2.38 Å and one phosphorous atom with a Ag–P distance of 2.326 Å. The crystal structure of **II** is formed by infinite rows of $[Ag(Phen)_2]^+$ cations between which $[CF_3COO]^-$ anions are arranged. Relations between volatility and crystal structures of **I** and **II** are discussed.

Keywords: Silver carboxylates complexes; Crystal structures; Thermal analysis

1. Introduction

During the last 10 years, chemistry of volatile compounds has progressed rapidly due to an increasing interest in the use of these compounds as precursors for MOCVD thin film production [1]. A search for a suitable volatile silver precursor is a rather difficult task, since most silver coordination compounds have a polynuclear structure. They often possess low thermal stability and volatility and, as a rule, they are extremely light and moisture sensitive. In order to overcome the inherently low vapor pressure of silver coordination compounds, the formation of mononuclear adducts with neutral ligands is now widely used. The largest number of precursors which have been examined are the adducts of silver hexafluoroacetylacetonate (Hhfa) with neutral ligands (Q) which have the general formula [Ag(hfa)Q]. The thermal stability and volatility of such species are strongly influenced by the nature of the ligand Q and especially by the electronic nature of the heteroatom through which the ligand Q is coordinated by the silver ion.

It is known that silver forms rather strong bonds with the phosphorus(III) atom [2]. Therefore, the formation of an adduct with alkylphosphines can be advantageous for the enhancement of thermal stability and volatility of silver coordination compounds. Indeed, such adducts as $[Ag(hfa)(PR_3)]$ (R = Me, Et) have mononuclear structures and sublime under vacuum without decomposition [1] in contrast to the low volatile parent oligomeric β-diketonates [Ag(dik)] (dik = hfa; 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octadione (fod)) [3].

The search for suitable volatile silver precursors has been accomplished among silver carboxylates too. Mass-spectrometry data for some silver carboxylates indicate that they can be sublimed in vacuum [4–6]. For example, silver trifluoroacetate was used as MOCVD precursor [5]. However, it does not sublime easily and requires unconventional vaporization techniques [7]. More recently, a detailed mass-spectrometry study of two volatile carboxylates, silver pivalate $Ag[C(CH_3)_3COO]$ and silver trifluoroacetate $Ag[CF_3COO]$ was published [8,9]. It was found that both carboxylates sublimed under vacuum, but their sublimation was

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accompanied by partial thermal decomposition The X-ray single crystal data [10] have shown these carboxylates to be polymeric and that accounts for their low volatility. We have examined [11] silver pivalate in the MOCVD experiments and obtained silver films of good quality without especial techniques in contrast to silver trifluoroacetate [7]. Thereupon, we have synthesized the adduct of silver pivalate with tri-*n*-butylphosphine—$Ag(P^nBu_3)[C(CH_3)_3COO]$ (**I**) and demonstrated by mass spectrometry [8] that this adduct is more volatile and thermaly stable than the parent silver pivalate.

Here, we report the data on the X-ray single crystal determination for $Ag(P^nBu_3)[C(CH_3)_3COO]$ (**I**) and a newly synthesized adduct of silver trifluoroacetate with *o*-phenanthroline—$Ag(Phen)_2[CF_3COO]\cdot H_2O$ (**II**). In the following, we discuss the influence of the adducts formation on volatility and thermal stability of silver carboxylates.

2. Experimental

2.1. General information

Analytically pure reagents $C(CH_3)_3COOH$, CF_3COOH, KOH, P^nBu_3, $Phen\cdot H_2O$, $AgNO_3$ from Merck were used. The C, H and N contents were determined by conventional elemental analysis. The silver content was determined titrimetrically with titrant solution of KSCN and $Fe(NH_4)(SO_4)_2$ as indicator with an accuracy of about 1%.

2.2. Synthesis

All operations were performed in a light protected glass container. $Ag[C(CH_3)_3COO]$ and $Ag[CF_3COO]$ were prepared according to the literature methods [10].

The adduct $Ag(P^nBu_3)[C(CH_3)_3COO]$ (**I**) was synthesized by the method described in [8]. $Ag[C(CH_3)_3COO]$ (0.1 mmole) was suspended in CCl_4 (25 ml) and P^nBu_3 (0.1 mmol) was slowly added. The reaction mixture was stirred in a closed flask for 2 h resulting in a clear greenish solution from which brownish-green crystals were precipitated during concentration in vacuum. Purification was performed by recrystallization from ether. Yield: ~75%. *Anal.* Calc. :C, 49.67; H, 8.76; Ag, 26.25. Found: C, 49.5; H, 9.2; Ag, 25.7%.

The adduct $Ag(Phen)_2[CF_3COO]\cdot H_2O$ (**II**) was synthesized by the reaction between Phen (0.25 mmol) and $Ag[CF_3COO]$ (0.1 mmol) dissolved in a warm water–ethanol solution. The mixture was stirred for 1.5 h. The yellow precipitate of **II** formed after cooling the reaction mixture to 0 °C and was recrystallized from ethanol. Yield: ~80%. *Anal.* Calc. :C, 52.12; H, 3.00; N, 9.35. Found: C, 52.6; H, 2.9; N, 9.1%.

IR spectra were recorded on a Perkin–Elmer 1600 FT IR spectrophotometer as Nujol and hexachlorobutadiene mulls between KBr plates. IR data (cm^{-1}): $Ag[C(CH_3)_3COO]$, 2990, 2880 (νCH_3), 1560, 1510sh ($\nu_{as}COO$), 1480, 1410, 1370 ($\nu_sCOO+\delta CH$); $Ag(P^nBu_3)[C(CH_3)_3COO]$ (**I**), 2990, 2940, 2910, 2880, 2840 ($\nu CH_3+\nu CH_2$), 1550, 1505sh ($\nu_{as}COO$), 1480, 1460, 1430, 1400, 1370, 1340 ($\nu_sCOO+\delta CH+\nu PC$); $Ag[CF_3COO]$, 1640, 1615 ($\nu_{as}COO$), 1450 (ν_sCOO), 1200, 1150 (νCF_3); $Ag(Phen)_2[CF_3COO]\cdot H_2O$ (**II**), 1630, 1615, 1605, 1590 ($\nu_{as}COO+Phen$), 1460 (ν_sCOO), 1200, 1150 (νCF_3), 840, 745 (Phen).

Thermogravimetric analyses were carried out under vacuum (0.01 Torr) on a Sinku–Riko TGD-7000 thermal analyzer at a heating rate of 10° min^{-1}. Isothermal vacuum sublimation experiments were done with 100 mg samples in glass test tubes for 30 min at 0.01 Torr. Weight losses were determined gravimetrically and controlled by titrimetric analyses of the sublimates.

2.3. Crystal structure determination

Suitable single crystals of $Ag(P^nBu_3)[C(CH_3)_3COO)]$ (**I**) and $Ag(Phen)_2[CF_3COO]\cdot H_2O$ (**II**) were obtained by slow evaporation of the ethanol and the ether solution, respectively.

Intensity data were collected on an image plate diffractometer (IPDS, Stoe) using monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Crystallographic data and some details of data collection and structure refinement are given in Table 1. Empirical absorption correction was applied for crystal of **II** using ψ-scans for four reflections. The structures were determined by a combination of direct methods (SHELXS-86) and Fourier syntheses and refined anisotropically (SHELXL-93) for all non-hydrogen atoms. H-atoms were placed in the calculated positions and refined isotropically in a riding mode.

3. Results and discussion

Adducts $Ag(P^nBu_3)[C(CH_3)_3COO]$ (**I**) and $Ag(Phen)_2[CF_3COO]\cdot H_2O$ (**II**) were obtained through interaction between solutions of parent silver carboxylate and additional neutral ligand. Silver carboxylates form adducts easily. They are non-hydroscopic and can be handled in air. However, they are light sensitive and have to be stored in a light protected container. Adduct **I** is soluble in non-polar organic solvents (ether, CCl_4, benzene). Compound **II** is soluble in ethanol.

The characteristic bands of carboxylate and neutral ligands are present in the IR spectra of adducts **I** and **II**. It is noticed that ($\nu_{as}COO$) are slightly shifted (by ~10 cm^{-1}) to low frequencies in comparison with the IR

Table 1
Crystal data and structure refinement for $Ag(P^nBu_3)[C(CH_3)_3COO]$ (**I**) and $Ag(Phen)_2[CF_3COO]\cdot H_2O$ (**II**)

	$Ag(P^nBu_3)[C(CH_3)_3COO]$	$Ag(Phen)_2[CF_3COO]\cdot H_2O$
Empirical formula	$AgC_{17}H_{36}O_2P$	$AgC_{26}H_{18}F_3N_4O_3$
Formula weight	411.30	599.31
Crystal system	monoclinic	monoclinic
Space group	*C2/c*	*C2/c*
a (Å)	23.488(6)	33.393(7)
b (Å)	11.986(3)	7.158(1)
c (Å)	18.168(5)	24.610(5)
β (°)	126.55(2)	127.71(3)
Volume (Å^3)	4109(2)	4654(2)
Z	8	8
D_{calc} (Mg m^{-3})	1.330	1.711
μ (Mo Kα), (mm^{-1})	1.062	0.928
Crystal size, (mm)	0.6 × 0.2 × 0.1	0.3 × 0.2 × 0.2
Temperature (K)	140(2)	180(2)
θ Range for data collection (°)	2–26	3–25
Reflections collected	4601	9844
Independent reflections	4033	3557
Data/restraints/parameters	2558/0/227	3539/36/329
Goodness-of-fit on F^2	1.076	0.850
R_1 [$I > 2\sigma(I)$]	0.0441	0.0519
wR_2	0.1359	0.1188
Largest difference peak and hole (e Å^{-3})	0.485 and −0.678	0.446 and −0.548

spectra of the parent silver carboxylates due to adduct formation. However, a detailed interpretation of the IR spectra of **I** and **II** is complicated by overlapping, main characteristic bands of the ligands. The formation of adducts **I** and **II** has been confirmed by X-ray crystallography.

In the crystal structure of **I** (Fig. 1), the $Ag(P^nBu_3)[C(CH_3)_3COO]$ molecules are associated in dimers by two intermolecular bonds, Ag(a)–O(2) (2.626 Å). The closest coordination environment of the silver atom consists of two oxygen atoms with the distances, Ag–O(1) 2.278 and Ag–O(2) 2.476 Å, and one phosphorous atom with the distance Ag–P 2.326 Å (Fig. 1). The Ag–P bond length is close to the Ag–O bond lengths (Table 2). This fact proves that silver forms strong bonds with phosphorous containing ligands due to the possibility of 4d electron transfer from silver to 3d levels of the phosphorous atom. The interaction between 4d-orbitals of silver and 3d-orbitals of phosphorous led to the formation of d_π bonds. As a result, the electron density of silver shifts to the acceptor phosphorous atom. This may prevent the coordination of the next phosphorous ligand in the opposite direction. The analogous relationships between Ag–O and Ag–P bond lengths were found earlier for silver β-diketonates adducts with PR_3 ligands (where R = Me, Et) [1]. The association of AgPivBu molecules into dimers is the reason for the non-equivalence of two Ag–O bonds within one molecule: the Ag–O(2) bond is longer than the Ag–O(1) bond. The formation of additional Ag(a)–O(2) bonds results in the deformation of the plane formed by Ag, O(1), O(2) and P atoms. The distance from the Ag atom to the (O(1), O(2), P) plane is 0.14 Å. The molecules in dimeric units are related by a two-fold axis. There are only van-der-Waals interactions between dimeric units. The X-ray structure data are in a good agreement with the mass-spectrometry data [8] which showed the vapor phase over **I** to consist mainly of dimeric molecules.

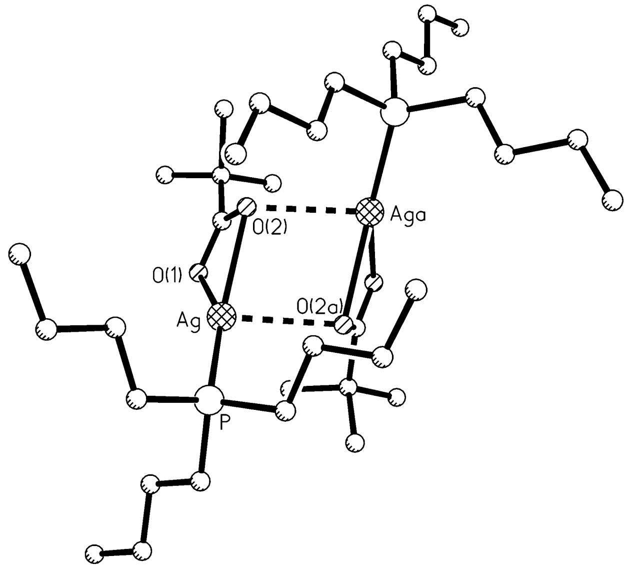

Fig. 1. Dimeric unit in the crystal structure of $Ag(P^nBu_3)[C(CH_3)_3COO]$ (**I**).

Table 2
Selected bond lengths in the crystal structures of $Ag(P^nBu_3)[C(CH_3)_3COO]$ (**I**) and $Ag(Phen)_2[CF_3COO]\cdot H_2O$ (**II**)

Compound	Bond	*D* (Å)
I	Ag–O(1)	2.278(4)
	Ag–O(2)	2.476(4)
	Ag–P	2.326(2)
	Ag(a)–O(2)	2.630(4)
II	Ag–N(1)	2.394(8)
	Ag–N(2)	2.334(14)
	Ag–N(3)	2.391(17)
	Ag–N(4)	2.387(9)

Comparing the crystal structures of **I** and parent $Ag[C(CH_3)_3COO]$, one should note that the introduction of a phosphorous containing ligand, which is able to accept silver d-electrons, destroys the polymeric $Ag[C(CH_3)_3COO]$ structure and leads to formation of a molecular crystal structure build up from discrete dimeric units. Moreover, the coordination mode of the carboxylic group and the coordination environment of silver changes considerably. In the crystal structure of $Ag[C(CH_3)_3COO]$, the carboxylic group acts as a tridentate bridging ligand, whereas this group appears as a chelate-briging tridentate in the crystal structure of **I**.

In the crystal structure of **II**, the closest coordination environment of silver consists of four nitrogen atoms from two *o*-phenanthroline molecules. As the π-acceptor properties of the *o*-phenanthroline molecule are weaker than those of the phosphine ligand, the electron shift from the silver atom to the one ligand is not so large. Possibly due to this fact the addition of another ligand molecule in the opposite direction is not complicated. Thus, the silver atom is able to coordinate two *o*-phenanthroline molecules with the formation of the $[Ag(Phen)_2]^+$ cations (Fig. 2). The Ag–N bond lengths in the $[Ag(Phen)_2]^+$ cations fall in the range of 2.33–2.39 Å (Table 2). Two Phen ligands from the one cation do not lie in the same plane and are twisted by the small angle of 32.4° (Fig. 3). Such an arrangement of *o*-phenanthroline molecules around the silver atom was found earlier in the structure of $[Ag(ocp)_2(PF_6)\cdot CH_2Cl_2]$ (ocp = octachloro-1,10-phenanthroline) [12]. Due to the presence of two large *o*-phenanthroline molecules, no free space in the silver coordination sphere is left and the organic $[CF_3COO]^-$ anion is moved off from the closest silver environment. It should be noted that a water molecule is arranged near the trifluoroacetate anions and connected with oxygen atoms by two hydrogen bonds. As it can be expected, there is a π–π-stacking interaction between Phen ligands of the neighbor $[Ag(Phen)_2]^+$ cations with a Phen–Phen interplanar separation of about 3.5 Å. Due to these interactions, the cations and therefore $[CF_3COO]^-$ anions, form infinite rows where the ions are arranged on each other with a slight shift (Fig. 2).

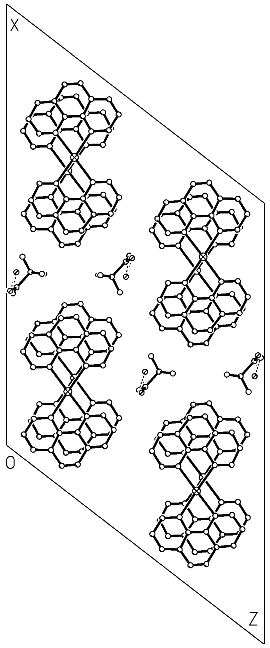

Fig. 2. The crystal packing of $Ag(Phen)_2[CF_3COO]\cdot H_2O$ (**II**). The infinite rows of $[Ag(Phen)_2]^+$ cations and $[CF_3COO]^-$ anions can be easily seen.

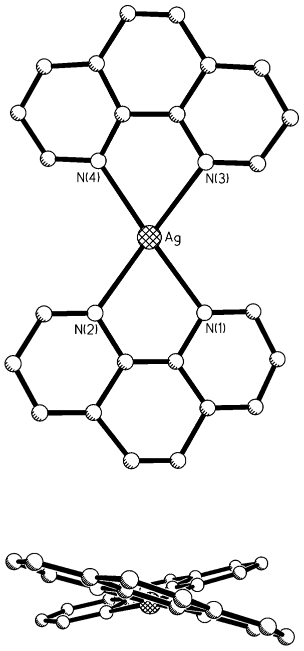

Fig. 3. A fragment of $Ag(Phen)_2[CF_3COO]\cdot H_2O$ (**II**) crystal packing. The 1,10-phenanthroline molecules from different cations are arranged in parallel planes. Two phen ligands of the cation are twisted by a small angle.

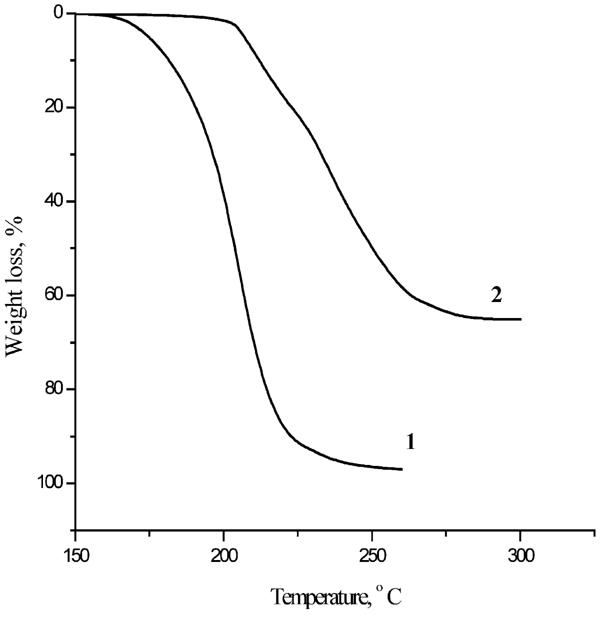

Fig. 4. TG-curves of $Ag(P^nBu_3)[C(CH_3)_3COO]$ (**I**) (1) and $Ag[C(CH_3)_3COO]$ (2) under vacuum.

The data of thermal analysis under vacuum shows that adduct **I** can be sublimed in the temperature range of 180–220 °C (Fig. 4, curve 1) in contrary to the parent carboxylate $Ag[C(CH_3)_3COO]$, for which sublimation is accompanied by a remarkable decomposition process (Fig. 4, curve 2). The experiments on vacuum sublima-

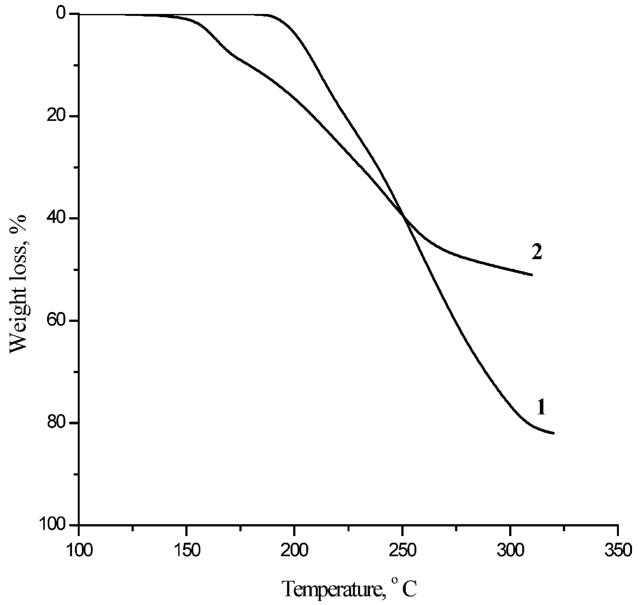

Fig. 5. TG-curves of Ag(Phen)$_2$[CF$_3$COO]·H$_2$O (**II**) (1) and Ag[CF$_3$COO] (2) under vacuum.

tion show that the sublimation of **I** occurs at 180 °C at 0.01 Torr and complete mass loss is observed. It is a remarkable difference from the parent Ag[C(CH$_3$)$_3$COO] which sublimes at a higher temperature (240 °C compared with 180 °C for **I**).

The thermogravimetric analysis curves for **II** and the parent Ag[CF$_3$COO] are shown in Fig. 5. A weight loss occurs at 200–310 and 160–300 °C, respectively, for **II** and Ag[CF$_3$COO]. The values of weight loss correspond to decomposition of these complexes with formation of silver (82% is calculated for **II** and 51% for Ag[CF$_3$COO]). At 240 °C in vacuum, Ag[CF$_3$COO] sublimes with partial thermal decomposition. Compound **II** does not possess any volatility and decomposes at 0.01 Torr in the temperature range of 150–250 °C. This fact can be easily understood taking into account the ionic nature of the crystal structure of the compound.

In conclusion, the formation of adducts with neutral ligands does not always increase the volatility of the complexes. In the complex with tributylphosphine, the formation of polymeric carboxylic chains is prevented, which results in the molecular crystal structure built up from discrete dimeric units. Therefore, Ag(P^{n}Bu$_3$)[C(CH$_3$)$_3$COO] is more volatile than the parent Ag[C(CH$_3$)$_3$COO]. The complex with *o*-phenanthroline has an ionic structure, [Ag(Phen)$_2$][CF$_3$COO]·H$_2$O, and this compound does not possess any volatility.

4. Supplementary material

The complete crystallographic data are available from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) on request, quoting the deposition numbers 182886 (**I**) and 182887 (**II**).

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