THERMAL BEHAVIOUR OF DIMETHYLGOLD(III) CARBOXYLATES

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The thermal properties of dimethylgold(III) carboxylates of general formula $[(CH_3)_2Au(OOCR)]_2$ (*R*=methyl **(1)**, *tert*-buthyl **(2)**, trifluoromethyl **(3)**, or phenyl **(4)**) in solid state have been investigated by the thermogravimetric analysis. The temperature dependences of saturated vapour pressure of complexes have been studied by the Knudsen effusion method with mass spectrometric indication. The thermodynamic parameters $\Delta_{sub}H_T^o$ and $\Delta_{sub}S_T^o$ of the sublimation processes have been calculated. Thermal decomposition of the vapour of complexes **1** and **2** has been studied by means of high temperature mass spectrometry in vacuum, and by-products of decomposition have been determined.

Introduction

Metal organic chemical vapour deposition processes (MOCVD) are used for nano- and microelectronics applications [1–3]. Thermal properties of precursors play a critical role in MOCVD. Presently, little is known about thermal behaviour of precursors for gold MOCVD [4–6]. The investigation of thermal properties of the organogold compounds in the solid and gas phases within a broad temperature range is both of scientific and practical importance. We chose dimethylgold(III) carboxylates as the objects of investigation because of their high volatility and thermal stability. The substituent effect in the carboxylate ligand on thermal properties and on the volatility of the dimethylgold(III) carboxylates has been demonstrated.

In the present work we studied thermal properties of dimethylgold(III) acetate $[Me_2Au(OAc)]_2$ **(1)**, pivalate $[Me_2Au(piv)]_2$ **(2)**, trifluoroacetate $[Me_2Au(tfa)]_2$ **(3)**, and benzoate $[Me_2Au(OBz)]_2$ **(4)** (here *OAc*=$OOCCH_3$, *piv*=$OOCC(CH_3)_3$, *tfa*=$OOCCF_3$, *OBz*=$OOCPh$). Previously we carried out thermogravimetric analysis (TG) and measured temperature dependences of saturated vapour pressure (*P/T* dependences) for complexes **1** and **2** [7, 8]. In this paper the TG curves and the volatility of compounds **3** and **4** are shown. For complexes **1** and **2**, as the most promising MOCVD precursors, we studied the thermal decomposition processes of vapour in approximation to a single molecule. The use of a wide range of substituents allowed us to follow changes in the thermal stability and volatility of dimethylgold(III) carboxylates.

Experimental

The complexes $[(CH_3)_2Au(OOCR)]_2$ (*R*=Me **(1)**, *t*-Bu **(2)**, CF_3 **(3)**, Ph **(4)**) were synthesized in a single step reaction from $[(CH_3)_2AuI]_2$ and AgOOCR by the method described in detail in [7–9]. The compounds were purified by recrystallization from hexane. An elemental analysis, X-ray, IR, and ^1H NMR spectroscopy were used for characterization of compounds. The products are stable to moisture and air; they do not require special dry conditions for storage. The complexes **1–4** soluble in most common organic solvents, have a low melting point and sublimate at low temperatures in vacuum.

The thermal properties of the compounds in the solid phase were studied by means of TG using NETZSCH STA 409 PC/PG device. The experiments were performed in a helium flow (20–40 mL min^{-1}) with a heating rate of 10°C min^{-1} in the range of temperatures 50–350°C; standard open crucibles were used.

MI-1201 device was used to study the mass spectra of the gas phase of the complexes **2–4**. The energy of ionizing electrons was 35 eV. The vapour temperature of complexes was 40°C **(2)**, 45°C **(3)**, and 130°C **(4)**. Mass spectra of the complexes **1–4** are presented in Table 1. The mass spectrum of **1** was published in [7].

The saturated vapour pressure of the complexes was measured by the Knudsen effusion procedure combined with mass spectrometric analysis of the gas phase composition. The thermodynamic parameters of sublimation process $\Delta_{sub}H_T^o$ and $\Delta_{sub}S_T^o$ have been

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Table 1 Mass spectra of dimethylgold(III) carboxylates

m/z	Ion	$I_{rel}/\%$	m/z	Ion	$I_{rel}/\%$
	1[a]			**2**	
225	$[AuC_2H_4]^+$	7	423	$[Au_2C_2H_5]^+$	37
227	$[AuC_2H_6]^+$	8	527	$[(C_2H_8)Au_2O_2CC(CH_3)_3]^+$	90
409	$[Au_2CH_3]^+$	23	528	$[(C_2H_9)Au_2O_2CC(CH_3)_3]^+$	89
453	$[Au_2O_2CCH_3]^+$	100	554	$[(C_4H_{11})Au_2O_2CC(CH_3)_3]^+$	100
483	$[(CH_3)_2Au_2O_2CCH_3]^+$	42			
527	$[CH_3(AuO_2CCH_3)_2]^+$	7			
	3			**4**	
223	$[Au_2CH_2]^+$	20	223	$[AuC_2H_2]^+$	25
225	$[AuC_2H_4]^+$	10	225	$[AuC_2H_4]^+$	39
409	$[Au_2CH_3]^+$	37	273	$[AuC_6H_4]^+$	100
423	$[Au_2C_2H_5]^+$	16	288	$[AuC_7H_7]^+$	23
516	$[(C_2H_4)Au_2O_2CCF_2]^+$	13	348	$[(CH_3)_2AuO_2CC_6H_5]^+$	23
548	$[(CH_3)_4Au_2O_2CCF_2]^+$	100	409	$[Au_2CH_3]^+$	7
567	$[(CH_3)_4Au_2O_2CCF_3]^+$	70	477	$[C_3H_3AuO_2C]^+$	79
			524	$[(CH_3)_4Au_2O_2CCH_2]^+$	72
			545	$[(CH_3)_2Au_2O_2CC_6H_5]^+$	39
			575	$[(CH_3)_4Au_2O_2CC_6H_5]^+$	6
			625	$[(C_2H_9)Au_2O_2C(C_6H_5)_2]^+$	27
			666	$[(CH_3)_2Au_2(O_2CC_6H_5)_2]^+$	19

[a]the data of [7]

Table 2 Thermodynamics parameters of sublimation process of dimethylgold(III) carboxylates

Complex	m.p./°C	No. of points	$\log P/\text{Torr}=A–B/T$, K A	$\log P/\text{Torr}=A–B/T$, K $B\cdot10^{-3}$	Temp. range/ °C	$\Delta H_T^\circ/$ kJ mol^{-1}	$\Delta S_T^\circ/$ J mol^{-1} K^{-1}
1[a]	95–96	7	14.2±0.1	5.28±0.04	18–49	100.9±0.8	216.7±1.5
2[b]	75–76	8	15.3±0.4	5.70±0.11	22–50	109.1±2.1	273.1±7.1
3	102–103	6	14.9±0.5	5.42±0.15	23–52	103.6±2.9	229.9±7.7
4	185–187	4	17.7±0.2	8.08±0.08	90–130	154.5±1.5	283.4±3.2

[a]the data of [7], [b]the data of [8]

calculated. Temperature dependences of vapour pressure as the equation $\log P=A–B/T$ and thermodynamic data are showed in Table 2. Detailed description of the measurement method and experimental technique is presented in [10].

The thermal decomposition process of the vapour of compounds **1** and **2** on a heated substrate was studied by means of high temperature mass spectrometry. The complexes were transferred to the gas phase at a temperature as chosen using P/T dependencies in a manner to provide equal mass transfer for each substance. The vapour pressure of complexes under investigation was low (~10^{-4} Torr). Detailed description of the method and setup can be found in [11].

Results and discussion

Thermogravimetric analysis

TG analysis in this work was used for the preliminary estimation of volatility properties of organogold complexes. The mass loss curves of dimethylgold(III) carboxylates are shown in Fig. 1. It was found that only complex **1** gets evaporated almost completely without decomposition (Fig. 1). The mass loss for **1** is 96% [7]. Complexes **2**, **3** and **4** get evaporated with partial decomposition; the corresponding mass losses are 88, 83 and 42%. The mass concentration of gold in compound **4** is 56%, so, according to the TG data, dimethylgold(III) benzoate completely decomposes at a temperature of about 200–250°C (Fig. 1). A qualitative volatility row for dimethylgold(III) carb-
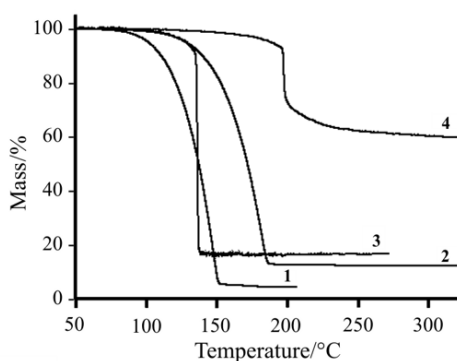
Fig. 1 TG curves of dimethylgold(III) carboxylates in He: [Me$_2$Au(OAc)]$_2$ **(1)** [7], [Me$_2$Au(piv)]$_2$ **(2)** [8], [Me$_2$Au(tfa)]$_2$ **(3)** and [Me$_2$Au(OBz)]$_2$ **(4)**

Fig. 2 Temperature dependences of saturated vapour pressure of dimethylgold(III) complexes: [Me$_2$Au(OAc)]$_2$ **(1)** [7], [Me$_2$Au(piv)]$_2$ **(2)** [8], [Me$_2$Au(tfa)]$_2$ **(3)** and [Me$_2$Au(OBz)]$_2$ **(4)**

oxylates was found (for 35% mass loss): **1** (124°C)> **3** (135°C)>**2** (156°C)>**4** (198°C). The TG data give only qualitative volatility series because the evaporation is accompanied by decomposition in many cases.

Mass spectrometry study

Analysis of the mass spectra of compounds **1–4** showed that dimethylgold(III) carboxylates are composed of dimer molecules in the gas phase (Table 1). The relative intensities of molecular ions in the mass spectra of **2–4** are less than 1%. The fragmentation processes are similar for dimethylgold(III) carboxylates (Table 1). The mass spectra of the compounds contain the peaks related to ions [Me$_4$Au$_2$L]$^+$, [Me$_2$Au$_2$L]$^+$ and [Au$_2$Me]$^+$, where *L*=carboxylate ligand. Molecular ions of complexes get fragmented with consecutive removal of methyl groups and carboxylate ligand.

Vapour pressure

The Knudsen effusion procedure with mass spectrometric analysis of the composition of gas phase was used to measure the temperature dependencies of the saturated vapour pressure (*P/T* dependencies) of complexes **1–4** (Fig. 2). From *P/T* dependences it was found that the most volatile compound of dimethylgold(III) carboxylate series within the temperature range 23–52°C is the fluorine-substituted complex **3** (Table 2, Fig. 2). An increase in vapour pressure was previously observed to accompany the introduction fluorine-containing substituents into the complexes of dimethylgold(III) with β-diketones [4]. The transition from dimethylgold(III) acetylacetonate to trifluoroacetylacetonate (substitution of one CH$_3$ group by CF$_3$) results in an increase in vapour pressure by a factor of 4 [4]. In the case of dimethylgold(III) hexafluoroacetylacetonate
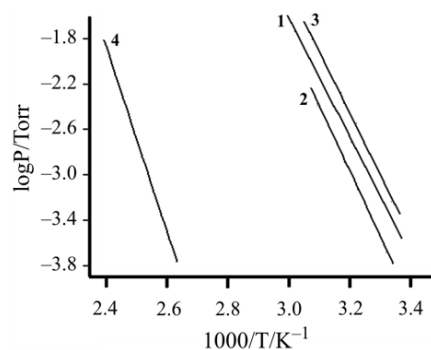
(substitution of two CH$_3$ group by CF$_3$) vapour pressure increases in 44 times [4]. A similar effect is also observed for other classes of the coordination compounds of metals [12, 13]. However, in the case of metals(II) and (III) β-diketonates, the transition to hexafluoroacetylacetonate increases the vapour pressure in 4–5 orders of magnitude [14]. Substitution of CH$_3$ group in compound **1** by CF$_3$ (complex **3**) causes only a 1.8 times increase in vapour pressure at a temperature of 37°C (Table 2, Fig. 2). Such a difference is likely to be connected with the effects of crystal packing in the investigated complexes. Substitution of the methyl group by *tert*-butyl in the carboxylate ligand (compounds **1** and **2**) causes a decrease in the volatility within the studied temperature range (Fig. 2). It should be noted that dimethylgold(III) dipivaloylmethanate and acetylacetonate have close vapour pressure values [6]. Complex **4** differs from other dimethylgold carboxylates by poor volatility (Fig. 2). This may be explained by a substantially larger molecular mass and by the presence of the aromatic system in the molecule of 4. Similar effects were observed previously for the complexes of zirconium(IV) [12] and aluminium(III) as examples [15].

Relative intensities of ions in the mass spectra did not change during the measurements of vapour pressure for compounds **1–4** within the investigated temperature ranges (Table 2). This proves that the complexes are thermally stable at this temperature. On the basis of *P/T* dependences the thermodynamic parameters of sublimation process have been calculated (Table 2). It is similar to $\Delta_{sub}H_T^\circ$ and $\Delta_{sub}S_T^\circ$ for dimethylgold(III) β-diketonates [6].

From *P/T* dependences the following volatility of dimethylgold(III) carboxylates row was found (for *P*=10^{-3} Torr): **3** (30°C)>**1** (34°C)>**2** (38°C)> **4** (117°C). These data are in good agreement with the qualitative volatility series from TG data. So, it was shown that the nature of the carboxylate ligand has a

substantial effect on the volatility of dimethyl-gold(III) carboxylates.

Thermal decomposition

Thermal decomposition of compounds **1** and **2** is shown in Figs 3 and 4. Preliminary data were reported by us previously in [8]. In the present work we considered the process of thermal decomposition of the compounds in more detail. On the basis of the analysis of thermal dependences of the main peak intensities in the mass spectra of thermolysis products, temperatures of decomposition start were determined for the complexes in the gas phase. Under the experimental conditions, thermolysis of the molecules starts at a temperature above 65±5°C for **1** and 60±5°C for **2** (Figs 3, 4). Substitution of the methyl group of acetate ligand in **1** by the *tert*-butyl group leads to decrease in the threshold temperature of vapour decomposition. The main volatile organic products of thermolysis of complex **1** are represented by fragments $COCH_2$, $OOCCH_3$ and C_2H_6 (Fig. 3), for **2** – $COCH$, $C_3H_5OOCC(CH_3)_3$, pivalic acid, and C_2H_6 (Fig. 4). The mechanisms of thermal decomposition of **1** and **2** are alike. For both compounds, the corresponding carboxylic acid and ethane are among the main thermolysis products. Under the experimental conditions, complex **2** has slower kinetics of thermodecomposition than **1** (Figs 3, 4). This data can be used for choice of the MOCVD parameters to gold material deposition.

Conclusions

In the present work we demonstrated the influence of various substituents in the complexes of dimethyl-gold(III) with carboxylic acids on their volatility and thermal behaviour. The most volatile compound of the investigated series of dimethylgold(III) carboxylates is dimethylgold(III) trifluoroacetate $[Me_2Au(tfa)]_2$. The volatility row for dimethylgold(III) carboxylates was found from P/T dependences: $[Me_2Au(tfa)]_2>$ $[Me_2Au(OAc)]_2>[Me_2Au(piv)]_2>[Me_2Au(OBz)]_2$; this row coincides with the qualitative volatility row arranged on the basis of TG data. The main thermo-dynamic characteristics of complex sublimation processes were determined. It was shown that the temperature of decomposition start for dimethylgold(III) acetate vapour is higher than that for dimethylgold(III) pivalate. A carboxylic acid and ethane are among the main products of thermolysis of dimethylgold(III) carboxylates.
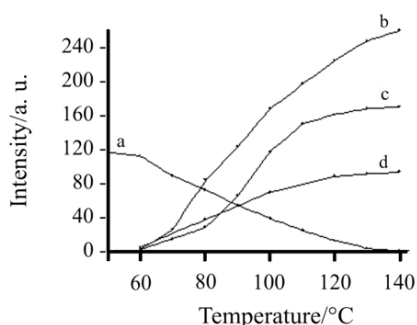

Fig. 3 Temperature dependence of intensities of ion peaks at decomposition of $[Me_2Au(OAc)]_2$ **(1)**; general ions: a – $[Au_2(OOCCH_3)]^+$ (453 *m/z*), b – $[COCH_2]^+$ (42 *m/z*), c – $[OOCCH_3]^+$ (59 *m/z*), d – $[C_2H_6]^+$ (30 *m/z*)
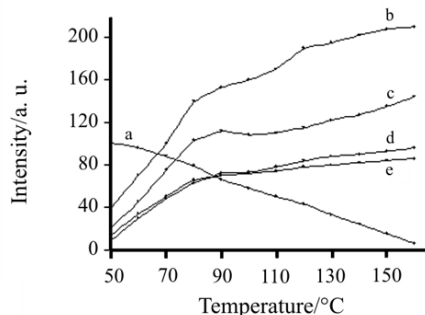

Fig. 4 Temperature dependence of intensities of ion peaks at decomposition of $[Me_2Au(piv)]_2$ **(2)**; general ions: a – $[(C_4H_{11})Au_2OOCC(CH_3)_3]^+$ (554 *m/z*), b – $[COCH]^+$ (41 *m/z*), c – $[(C_3H_5)OOCC(CH_3)_3]^+$ (142 *m/z*), d – $[HOOCC(CH_3)_3]^+$ (102 *m/z*), e – $[C_2H_6]^+$ (30 *m/z*)

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