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Copper(I) complexes as potential CVD precursors – studies in the liquid state and gas phase*

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Cu(I) complexes with trimethyl phosphite and aliphatic perfluorinated carboxylates of the type $[Cu_2\{P(OMe)_3\}_2(\mu\text{-}RCOO)_2]$ where R = CF_3, C_2F_5, C_3F_7, C_6F_{13}, C_7F_{15}, C_8F_{17}, C_9F_{19} have been prepared as viscous liquids. The spectroscopic results suggest the dimeric structures for complexes in the liquid state, where the metal ions are linked by the bridging carboxylates. This type of bonding was revealed in the gas phase as well. In mass spectra the most intensive signals were observed for the $[Cu_2(RCOO)]^+$ and $[Cu_2(RCOO)_2]^+$ fragments. Thermal decomposition of complexes proceeds as a multistage process, yielding a Cu_2O in the most of cases.

Key words: *Cu(I) complexes, CVD precursors, trimethyl phosphite, perfluorinated carboxylates, TGA*

1. Introduction

Previous studies revealed that gold(I) and silver(I) complexes with perfluorinated carboxylates and tertiary phosphines presented a sufficient volatility for chemical vapour deposition (CVD) [1–5], hence the purpose of this work was to prepare volatile precursors for CVD of copper metal or copper oxide thin films. The EI mass spectrometry, temperature-variable IR spectroscopy and thermal studies were undertaken to determine the kind of species occurring in the gas phase and the mechanism of the reaction of thermal decomposition. The knowledge about the structural and thermal properties should ascertain the suitability of complexes as precursors for CVD, which ought to be competitive to organometallics used at present.

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2. Experimental section

2.1. Materials

Trimethyl phosphite (98%), perfluorinated carboxylic acids (97–99%) and copper powder for organic synthesis were purchased from Aldrich and used without further purification. Acetonitrile of analytical grade (Fluka) was dried over molecular sieves 4A, next over CaH_2 and, finally, was distilled under dry nitrogen from P_4O_{10} prior to use.

2.2. Methods

Thermal studies were performed with a MOM OD-102 Derivatograph (Paulik and Paulik, Hungary). The atmosphere over the sample was nitrogen; the heating range 293–773 K, heating rate 2.5 K/min, sample mass 40–200 mg, the TG range 50, 100 or 200 mg and the reference material Al_2O_3. Powder diffractograms were recorded with an HZ64/A-2 DRON-1 diffractometer using CuK_α radiation, $\lambda = 0.1542$ nm. Mass spectra were recorded on an AMD-640 mass spectrometer using the EI method in the range of 293–573 K. Temperature-variable IR spectra (4000–400 cm^{-1}) were performed with a Perkin–Elmer 2000 FT IR spectrophotometer in the range of 296–463 K, at the pressure of 10^{-2} mbar. Copper was determined using a Carl Zeiss Jena AAS spectrometer with $Cu(NO_3)_2$ solution as the standard.

2.3. Synthesis

The reactions were performed under argon atmosphere using Schlenk techniques. Suitable copper(II) carboxylates $(RCOO)_2Cu$ were synthesised as described in [6]. In the general procedure, copper(II) carboxylate ($3.0\cdot10^{-3}$ moles) was placed in the Schlenk tube, either dissolved or suspended in 45 cm^3 of freshly distilled acetonitrile and copper powder ($9.0\cdot10^{-3}$ moles) was added. The suspension obtained was stirred until the solution became pale yellow. Next, $P(OMe)_3$ ($6.0\cdot10^{-3}$ moles) in acetonitrile (6 cm^3) was added and the reaction mixture stirred for about 12 h at ambient temperature, filtered and the solvent evaporated on vacuum line, leaving pale yellow viscous liquid. The obtained complexes were unstable in air, turning green. The results of Cu determination were as follows (%) (calc./found):

(**1**) $C_{10}H_{18}Cu_2F_6O_{10}P_2$, Cu (21.2/21.8); (**2**) $C_{12}H_{18}Cu_2F_{10}O_{10}P_2$, Cu (18.1/18.4);
(**3**) $C_{14}H_{18}Cu_2F_{14}O_{10}P_2$, Cu (15.9/15.8); (**4**) $C_{20}H_{18}Cu_2F_{26}O_{10}P_2$, Cu (11.5/11.0);
(**5**) $C_{22}H_{18}Cu_2F_{30}O_{10}P_2$, Cu (10.6/10.4); (**6**) $C_{24}H_{18}Cu_2F_{34}O_{10}P_2$, Cu (9.8/9.3);
(**7**) $C_{26}H_{18}Cu_2F_{38}O_{10}P_2$, Cu (9.1/9.0).

The EI mass spectra were recorded for the complexes in order to prove the formulae. The fragments confirming the stoichiometric composition were as follows: $[Cu_2(RCOO)]^+$, $[Cu_2(RCOO)_2]^+$, $[Cu_2(RCOO)\{P(OMe)_3\}]^+$ and $[Cu_2(RCOO)\{P(OMe)_3\}_2]^+$. For the particular complexes they were detected at ([m/z]): (**1**) 239, 352, 363, 487; (**2**) 289, 452, 413, 537; (**3**) 339, 552, 463, 587; (**4**) 489, 852, 613, 737; (**5**) 539, 952, 663, 787; (**6**) 589, 1052, 713, whereas for (**7**) only $[Cu_2(RCOO)]^+$ – 639 and $[Cu_2(RCOO)\{P(OMe)_3\}]^+$ – 763 were observed.

3. Results and discussion

3.1. Thermal analysis

The results of thermal analysis are given in Table 1. The examination of the thermoanalytical curves suggests a two-stage, exothermic decomposition process of complexes **2**–**6**, three-stage in the case of **7** and four-stage for complex **1**. The onset temperature of the first exoterm is in the range 298–303 K, suggesting that the perfluorinated chain had a small influence on the thermal stability of complexes studied.

Table 1. Results of the thermal analysis (in Nitrogen)

Compound	Heat effect	Temperature range[a] [K]			Weight loss on TG [%]		Detached group	Final product
		T_i	T_m	T_f	Found	Calc.		
(**1**) $[Cu_2\{P(OMe)_3\}_2(\mu\text{-}CF_3COO)_2]$	exo	303	343	403	27.9			
	exo	403	438	443	10.7	38.6		
	exo	443	468	478	26.4			
	exo	478	493	723	11.1	37.6	$2CF_3COO$	Cu_2O
(**2**) $[Cu_2\{P(OMe)_3\}_2(\mu\text{-}C_2F_5COO)_2]$	exo	298	348	448	35.1	35.6	$2P(OMe)_3$	
	exo	448	488	543	44.2	44.1		Cu_2O
(**3**) $[Cu_2\{P(OMe)_3\}_2(\mu\text{-}C_3F_7COO)_2]$	exo	298	308	353	20.6			
	exo	353	478	508	61.3	82.2		Cu_2O
(**4**) $[Cu_2\{P(OMe)_3\}_2(\mu\text{-}C_6F_{13}COO)_2]$	exo	298	323	398	22.9	22.5	$2P(OMe)_3$	
	exo	398	458	663	63.7	64.5		Cu_2O
(**5**) $[Cu_2\{P(OMe)_3\}_2(\mu\text{-}C_7F_{15}COO)_2]$	exo	298	398	413	21.9			
	exo	413	483	618	63.1	84.8	[c]	$3Cu_2O : Cu_2P_2O_7$
(**6**) $[Cu_2\{P(OMe)_3\}_2(\mu\text{-}C_8F_{17}COO)_2]$	exo	298	423	458	73.3			
	exo	458	468	518	15.3	89.0	[c]	Cu_2O
(**7**) $[Cu_2\{P(OMe)_3\}_2(\mu\text{-}C_9F_{19}COO)_2]$	exo	298	333	363	18.0	17.7	$2P(OMe)_3$	
	exo	373	493	563	69.4			
	exo	563	653	693	4.9	72.1[b]		Cu_2O

[a] T_i – initial temperature, T_m – maximum temperature, T_f – final temperature.

[b] Decomposition connected with the sublimation.

[c] Unable to determine.

In the case of compounds **2**, **4** and **7,** analysis of the thermogravimetric (TG) curves indicates dissociation of two molecules of phosphite in the first step. Moreover, detachment of the carboxylates residues in the last two stages can be proposed for **1**. In the case of complex 7, the second and third decomposition process was connected with the sublimation, probably resulting in the formation of $[Cu_2(C_9F_{19}COO)]$ or $[Cu_2(C_9F_{19}COO)_2]$ fragments. Decomposition reactions of compounds (**1** – **7**) were completed in the range of 508–723 K and the final product appeared to be Cu_2O. Only for the complex **5** a mixture of Cu_2O and $Cu_2P_2O_7$ (3 : 1) was observed. Powder diffractograms of the final products revealed lines for Cu_2O – 0.246, 0.214 nm that correspond to those reported in Powder Diffraction File [7]. IR spectra of the final product of **5** revealed strong vibrations in the range of 1065–1071 cm^{-1} that are characteristic of $Cu_2P_2O_7$ [8]. Similar final products were reported for other copper(I) phosphine complexes, e.g. $[Cu\{P(C_6H_5)_3\}_4]BF_4$ and $[Cu_2\{(P(OPh)_3\}_2(\mu\text{-}RCOO)_2]$ [6, 9]. The temperatures of the final product formation (T_f) were altered irregularly for the perfluorinated chains from C_1 to C_9 and in most cases these are in the range acceptable for CVD purposes with the hot wall reactor (625 K).

3.2. Mass spectrometry

Because the natural abundance of copper is ^{63}Cu (69.1 %) and ^{65}Cu (31.9 %), in compounds having one copper atom two signals can be expected with the intensity ratio 2:1. Species with two copper atoms should reveal three peaks with the characteristic 4:4:1 intensity pattern. As an example, the mass spectrum of **4** is presented in Fig. 1.

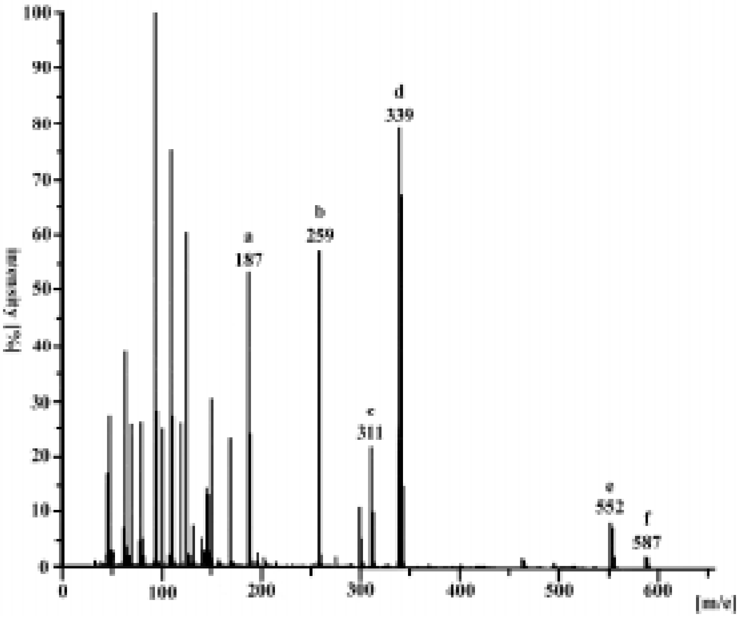

Fig. 1. EI mass spectrum of the complex $[Cu_2\{P(OMe)_3\}_2(\mu\text{-}C_3F_7COO)_2]$ (**3**): a) $[Cu\{P(OMe)_3\}]^+$, b) $[C_3F_7COOPMe]^+$, c) $[Cu\{P(OMe)_3\}_2]^+$, d) $[Cu_2(C_3F_7COO)]^+$, e) $[Cu_2(C_3F_7COO)_2]^+$, f) $[Cu_2(C_3F_7COO)\{P(OMe)_3\}_2]^+$

The analysis of the spectra suggests a dimeric structure for the compounds studied and points to the fragmentation scheme shown in Fig. 2.

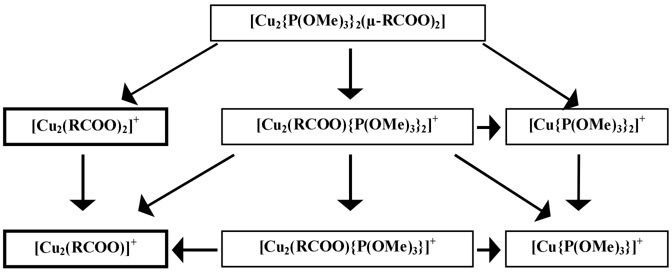

Fig. 2. Fragmentation scheme for the complexes $[Cu_2\{P(OMe)_3\}_2(\mu\text{-}RCOO)_2]$

Among the fragments including copper, the highest intensity was exhibited by $[Cu_2(RCOO)]^+$. The maximum intensity of this fragment varied and for **1** 10% was reached at 441 K, for **3** – 79% at 435 K and 100% in the case of **2** (409 K), **4** (301 K), **5** (470 K), **6** (362 K), **7** (497 K). The lower temperatures were observed for the complexes **2**, **4** and **6** containing the even number of carbons in the carboxylate chain. The compound **4** having the lowest temperature was studied using temperature-variable IR spectroscopy.

3.3. Temperature-variable IR

Temperature-variable IR spectra (296–463 K) recorded for the complex **4** are shown in Fig. 3. Among the bands characteristic of **4** we have chosen: 1682 cm^{-1}

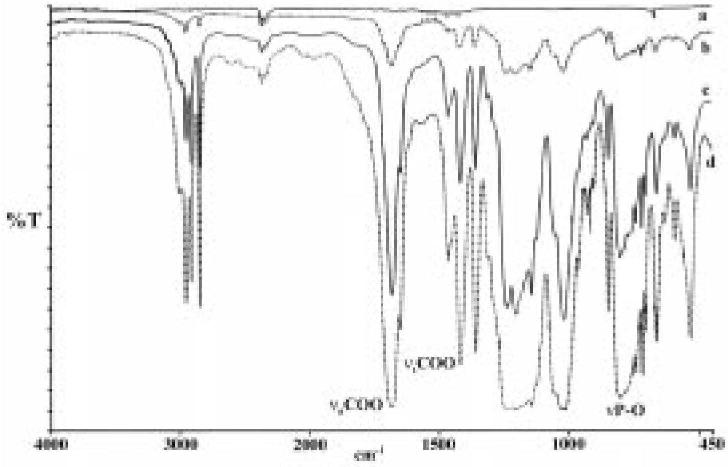

Fig. 3. Temperature-variable IR spectra of $[Cu_2\{P(OMe)_3\}_2(\mu\text{-}C_6F_{13}COO)_2]$ (**4**): a) $t = 0$ min, $T = 296$ K; b) $t = 30$ min, $T = 343$ K; c) $t = 71$ min, $T = 413$ K; d) $t = 86$ min, $T = 463$ K; t – time, T – temperature

(ν_aCOO), 1417 cm^{-1} (ν_sCOO) and 804 cm^{-1} (νP-O) [10, 11]. Because only the intensity of these bands was increasing during heating, we conclude that only the molecular form of $[Cu_2\{P(OMe)_3\}_2(\mu\text{-}C_6F_{13}COO)_2]$ (**4**) was present in the gas phase. Therefore the complex can be transported as a vapour to the CVD reaction chamber.

4. Conclusions

The thermal analysis data suggests that the compounds studied can be used in CVD of copper oxide films. The decomposition product can be modified however depending on the conditions of the deposition technique. The mass spectra and temperature-variable IR data analysis pointed to $[Cu_2\{P(OMe)_3\}_2(\mu\text{-}C_6F_{13}COO)_2]$ (**4**) as the most suitable potential liquid CVD precursor among the complexes studied.

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