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Gaseous phase studies of new copper(II) carboxylate complexes with *tert*-butylamine as potential precursors for chemical vapor deposition (CVD)

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ABSTRACT

Copper(II) carboxylate compounds with *tert*-butylamine of the general formula $[Cu_2(^tBuNH_2)_2(\mu\text{-}O_2CR)_4]$, where $R = C_nF_{2n+1}$, $n = 1–6$, were synthesized in the reaction of copper(II) perfluorinated carboxylates with *tert*-butylamine generated *in situ* from *tert*-butyl isocyanate. The obtained complexes were characterized in the solid state and in the gaseous phase by electron impact mass spectrometry (EI MS), IR spectroscopy, and thermal analysis with the detection of evolved gases. In addition, during the recrystallization of the $[Cu_2(^tBuNH_2)_2(\mu\text{-}O_2CC_3F_7)_4]$ complex the $(^tBuNH_3)^+(C_3F_7CO_2)^-$ ion pair was isolated, and its X-ray structure was determined. As a result of a mass spectra analysis, the presence of metallated species in the gaseous phase was revealed. Among the species detected, the pseudomolecular ions $[Cu_2(^tBuNH_2)_2(\mu\text{-}O_2CR)_3]^+$ were found. The fact confirmed the dimeric structure of the studied complexes with bridging carboxylates and axially N-coordinated amines. TGA studies demonstrated that copper transfer to the gaseous phase occurs at atmospheric pressure, which suggests that the obtained compounds can be promising precursors for chemical vapor deposition. The selected Cu(II) compounds were used in the preliminary CVD experiments, and the conformal copper layers were formed with no additional reducing agents.

1. Introduction

Copper is an important material commonly used in the advanced metallization of microelectronic and optoelectronic devices and ultralarge-scale integrated (ULSI) circuits due to its low electrical resistivity, high stress-induced deformation, and electromigration resistance higher than for aluminum. A synthesis and characterization of copper organometallic and coordination compounds as new precursors for chemical vapor deposition (CVD) of metallic nanolayers are an attractive topic for research [1–4]. A production of thin metal films using CVD techniques is a matter of interest due to advantages such as: the kinetically controlled deposition process, the conformal coverage, and the possibility of selective deposition. Precursors used in CVD influence the deposition process, morphology, structure, and physicochemical properties of the deposited layers [1,5]. Therefore, the synthesis and the selection of compounds which can be applied as precursors in CVD methods is the scope of the presented work. The selection of promising compounds is based on their thermal decomposition mechanisms, the ability to generate the volatile species, and the stability of the metallated species in the gaseous phase during transport.

In the case of Cu(I) precursors, they undergo the disproportionation reaction to metallic copper and copper(II) species (e.g. [Cu(β-diketonate)(L)], [Cu(β-ketoiminate)(L)], and $[Cu(\eta^5\text{-}C_5H_5)(L)]$; L = tertiary phosphines, unsaturated silanes, cyclooctadienes [1,4,6–13]). Most often however, copper(I) compounds are air and moisture sensitive and require special conditions during preparation, application, and storage. On the other hand, copper(II) compounds (e.g. [Cu(β-diketonate)$_2$] [1], [Cu(β-ketoiminate)$_2$] [14]) are more "user friendly", but an additional reducing agent (e.g. H_2) is necessary for the reduction of Cu(II) to Cu(0) during the CVD process. Therefore, compounds combining the advantages of Cu(II) and Cu(I) precursors are most attractive.

In our previous Cu(I) carboxylate precursors studies [15] attempts to isolate copper carboxylate complexes with alkyl isocyanates were made. However, products oxidized to green–blue species extremely easily. Therefore, a direct reaction between copper(II) perfluorinated carboxylates and *tert*-butyl isocyanate was performed and blue, crystalline compounds were readily separated. Nevertheless, the problem of these complexes composition and structure was not trivial (*vide infra*).

Alkyl isocyanates (RNCO) can react with nucleophiles, e.g. water, alcohols, and amines forming amines, urethanes, and imides, respectively [16]. Moreover, copper(II) compounds, e.g. β-diketonates can act as catalysts in the reaction of urethanes formation but a simple isocyanate coordination can also occur

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[17,18]. Therefore, the determination of the secondary ligand was an important problem in the isolated Cu(II) complexes. Furthermore, in the case of carboxylate compounds, miscellaneous structures (e.g. dimeric, tetrameric or more complicated ones) can be achieved. The above reasons make the determination of the composition and structure of the studied compounds an interesting issue.

On the other hand, various Cu(II) carboxylate compounds with amines were described [19,20] but the literature data for copper carboxylate compounds with simple aliphatic amines are very scarce. To the best of the Author's knowledge, there is one report on the crystal structure of the complex with methylamine and dicarboxylate: $[Cu(CH_3NH_2)(C_2O_4)]_n$ [21]. Additionally, the crystals were formed as a minor product in the mass of the predominant substrate $[Cu(ox)]\cdot0.33H_2O$. Therefore, a method of Cu(II) carboxylate complexes with simple aliphatic amines preparation has not been proposed (so far).

In this paper, the synthesis, electron impact mass spectra, thermal studies, and potential applications of $[Cu_2(^tBuNH_2)_2(\mu\text{-}O_2CR)_4]$ compounds where $R = C_nF_{2n+1}$, $n = 1–6$, will be described. Moreover, the X-ray structure of the $(^tBuNH_3)^+(C_3F_7CO_2)^-$ ion pair will be presented.

2. Experimental

2.1. Materials

$CuCO_3\cdot Cu(OH)_2$, *tert*-butyl isocyanate ^tBuNCO (97%), *tert*-butylamine $^tBuNH_2$ (97%), acetonitrile (99.93%), CF_3COOH (99%), and RCOOH (97%) ($R = C_nF_{2n+1}$; $n = 2–6$) were purchased from Aldrich, and used as received. Copper(II) carboxylates $[Cu(O_2CR)_2]$, where $R = C_nF_{2n+1}$, $n = 1–6$, were prepared as reported [22]. Acetonitrile for the direct experiment with *tert*-butylamine was dried and deoxygenated by standard methods.

2.2. Instrumentation

Mass spectra were detected with a Finnigan MAT 95 mass spectrometer, using electron ionization (EI) method over the temperature range 303–573 K. IR spectra were measured with a Perkin-Elmer Spectrum-2000 FT–IR spectrometer and a Spectrum RXI Perkin Elmer, using KBr (400–4000 cm^{-1}) and polyethylene discs or plates (100–400 cm^{-1}). The Cu content was determined with a Carl–Zeiss Jena AAS spectrophotometer. Thermal studies (TGA/DTA) were performed on a SDT 2960 TA analyzer for (**1**), (**2**) and (**6**) (dry N_2; heating rate – 2.5°min^{-1}, heating range up to 773 K; sample mass 6–13 mg) and a MOM OD-102 Derivatograph for (**3**–**5**) (the same conditions, sample mass 50 or 100 mg). Gaseous products of the thermal decomposition (TGA/DTA) of (**2**) were detected by a FT IR BioRad Excalibur spectrometer equipped with a thermal connector (T_L = 423 K) for gases.

2.3. Single-crystal structure determination

The single-crystal diffraction data for the $(^tBuNH_3)^+(C_3F_7CO_2)^-$ ion pair (**3b**) were collected on an Oxford Sapphire KM4 CCD diffractometer. The reflections for a colorless crystal of 0.20 × 0.20 × 0.08 mm dimensions were measured [23]. The compound structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 with the SHELXL program [24,25]. The numerical absorption correction was applied [23]. All the heavy atoms were refined with anisotropic thermal displacement parameters. Positions of hydrogen atoms attached to carbon atoms were assigned at calculated positions and refined with isotropic thermal displacement parameters fixed to a value 50% higher than those of the corresponding carbon atoms. Hydrogen atoms of the amino group were found from the electron density synthesis and refined with isotropic thermal displacement parameters fixed to a value 50% higher than that of nitrogen atoms, to which they are attached. In the anions, a permanent disorder was observed, i.e. positional for the both difluoromethylene groups and rotational for the terminal trifluoromethyl one. Hence, three constraints (DFIX) were applied on C–C and C–F bond lengths. A substantial increase in thermal displacement parameters for fluorine atoms was also observed. Carbon atoms demonstrated the disorder as well. All the figures were prepared in DIAMOND and ORTEP-3 [26,27]. The results of data collection and refinement were summarized in Table 1.

Table 1
Crystal data and structure refinement for the ion pair $(^tBuNH_3)^+(C_3F_7CO_2)^-$ (**3b**).

Empirical formula	$C_8H_{12}F_7NO_2$
Formula weight	287.19
T (K)	293(2)
λ (Å)	0.71073
Crystal system, space group	monoclinic, $P2_1/c$
Unit cell dimensions	
a (Å)	9.6445(8)
b (Å)	12.3278(9)
c (Å)	10.7588(8)
β (°)	100.877(7)
V (Å^3)	1256.20(16)
Z	4
D_{calc} (Mg/m^3)	1.518
Absorption coefficient (mm^{-1})	0.173
F(000)	584
Crystal size (mm)	0.20 × 0.20 × 0.08
θ Range for data collection (°)	2.54–25.68
Limiting indices	$-11 \leqslant h \leqslant 11$, $-14 \leqslant k \leqslant 15$, $-12 \leqslant l \leqslant 13$
Reflections collected/unique (R_{int})	8798/2370 (0.0275)
Completeness to θ = 25.68° (%)	99.9
Absorption correction	numerical
Transmission maximum/minimum	0.9863 and 0.9661
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	2370/3/234
Goodness-of-fit (GOF) on F^2	0.845
Final R indices [$I > 2\sigma(I)$][a]	R_1 = 0.0388, wR_2 = 0.0923
R indices (all data)[a]	R_1 = 0.0832, wR_2 = 0.1034
Largest diff. peak and hole (e Å^{-3})	0.195 and −0.123

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

2.4. CVD experiments

Preliminary deposition experiments were carried out using the horizontal *hot-wall* CVD reactor as described [28,29]. Copper films were deposited on Si(1 1 1) and Si/SiO_2, at 1.5 mbar pressure, in argon, within 60 min, at the vaporization temperature 473 K for (**1**) and (**5**), and 513 K for (**4**), whereas the substrate temperature values were between 663 and 713 K. The morphology and composition studies were performed using a scanning electron microscopy (SEM – LEO 1430VP, operating voltage 28 kV) equipped with energy dispersive X-ray spectrometer (EDS) Quantax 200 with detector XFlash 4010 (Bruker AXS microanalysis GmbH). XRD data were collected with a Philips X'PERT diffractometer. Diffractogramms were measured in 30–80° 2Θ ranges, using Cu Kα irradiation and sample spinning (step size – 0.1°, program. res. slit – 0.5, measuring time – 11 s per point).

2.5. Synthesis of $[Cu_2(^tBuNH_2)_2(\mu\text{-}O_2CR)_4]$) (**1**–**6**)

In the general procedure, copper(II) carboxylate $[Cu(O_2CR)_2]$ ($1\cdot10^{-3}$ mol for $R = CF_3$, C_2F_5, C_3F_7 or $0.5\cdot10^{-3}$ mol for $R = C_4F_9$, C_5F_{11}, C_6F_{13}) was dissolved in 20 cm^3 acetonitrile, and *tert*-butyl isocyanate in 5 cm^3 of acetonitrile ($1\cdot10^{-3}$ or $0.5\cdot10^{-3}$ mol,