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Polyfluorocarboxylates. I. Copper(II) trifluoroacetate and its analogues

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Abstract

A volatile complex of copper(II) trifluoroacetate with 1,4-dioxan has been obtained together with its acetate and trichloroacetate analogues. These compounds have been found to be convenient precursors for the metal organic chemical vapour deposition (MOCVD) technique for the synthesis of copper-containing thin films (including high-temperature superconducting films).

Keywords: Polyfluorocarboxylates; Trifluoroacetates; Copper(II) salts; 1,4-Dioxan complexes; Thin films; MOCVD

1. Introduction

The first representatives of the trifluoroacetates (TFA) of various metals were obtained by Swarts from aqueous solutions in the form of hydrates [1]. Their sensitivity towards air and moisture, and their ease of sublimation (in some cases) were noted. The latter property is quite important at present because of the increase in interest in volatile metal derivatives in general. One of the prospective areas for their practical application is the metal organic chemical vapour deposition (MOCVD) technique for the synthesis of high-temperature superconducting (HTSC) thin films from the Y–Ba–Cu–O and Bi–Ca–Sr–Cu–O systems. At present, the MOCVD method is based on volatile β-diketonates of the metals concerned [2–4], but as film precursors these compounds are not free from various disadvantages, e.g., the unsatisfactory characteristics of Ba, Sr and Ca derivatives and the complicated synthesis of the initial β-diketones. Hence the more readily available polyfluorocarboxylates (PFC) might provide convenient alternative precursors for the MOCVD process. The possibility of forming HTSC thin films from TFA has been already demonstrated using TFA solutions [5].

The purpose of the present work was the synthesis of the most simple compound of the Cu(II) PFC series, viz. $Cu(TFA)_2$, and the investigation of its behaviour as a film. To clarify the influence of fluorine atoms on the properties and volatility of $Cu(TFA)_2$, its acetate, $Cu(Ac)_2$, and trichloroacetate, $Cu(TCA)_2$, have also been investigated.

2. Experimental details

The synthesis of $Cu(TFA)_2 \cdot 2H_2O$ was carried out as reported previously [1].

Synthesis of dioxane complexes

The corresponding acid (0.1 mol) was mixed with 0.3 mol of copper hydroxocarbonate in a 250 ml flask and 150 ml of 1,4-dioxan were added. The solution was maintained for 10–12 h at 70 °C under magnetic stirring. Termination of the reaction was established by the absence of free acid in the solution probe after dilution with water. Excess carbonate was filtered off and 1,4-dioxan removed by distillation together with H_2O formed in the reaction. The products were recrystallized from toluene and sublimed; their yields and composition are listed in Table 1 together with the elemental analysis data of the sublimates.

Thin films of the compounds investigated were obtained on silicon substrates by vacuum evaporation.

Thermogravimetrical curves were recorded on a Setaram instrument at 10^{-3} Torr vacuum and a heating rate of 5 °C min^{-1}.

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Table 1
Composition and yields of compounds investigated

Compound	Yield (%)	Formula	Elemental analysis [found (calculated)] (%)			
			C	H	F[Cl]	Cu
I	99	$Cu(TFA)_2 \cdot 2H_2O$	14.90	0.93	34.93	19.2
		$C_4H_4F_6O_6Cu$	(14.72)	(1.22)	(34.97)	(19.6)
		sublimate	16.36	0.16	38.71	21.7
II	92	$2Cu(TFA)_2 \cdot C_4H_8O_2$	21.13	1.25	34.07	19.3
		$C_{12}H_8F_{12}O_{10}Cu_2$	(21.56)	(1.20)	(34.13)	(19.2)
		sublimate	21.41	1.16	33.91	19.3
III	90	$CuAc_2 \cdot C_4H_8O_2$	35.74	4.98	–	23.5
		$C_8H_{14}O_6Cu$	(35.56)	(5.19)	–	(23.7)
		sublimate	26.59	3.46	–	34.9
		$C_4H_6O_4Cu$	(26.37)	(3.30)	–	(35.2)
IV	94	$Cu(TCA)_2 \cdot 2C_4H_8O_2$	27.10	0.21	[40.01]	11.8
		$C_{12}H_{16}Cl_6O_6Cu$	(27.02)	(0.30)	(39.97)	(12.0)
		sublimate	12.19	–	[54.89]	16.2
		$C_4Cl_6O_4Cu$	(12.34)	–	(54.76)	(16.5)

3. Results and discussion

Our attempt to reproduce the synthesis of $Cu(TFA)_2$, as described previously [1], led to the formation of dark blue crystals with the composition $Cu(TFA)_2 \cdot 2H_2O$ (compound I; see Table 1). The thermogravimetric curves for this substance are presented in Fig. 1(a).

These show that a quite intensive decrease in mass had occurred already at 70–100 °C, the presence of peaks on the DTA curve indicating that the sublimation process was accompanied by the elimination of water molecules. This interpretation is also confirmed by the elemental analysis data of the sublimate of this compound (see Table 1). Complete thermal destruction of compound I occurred at 318 °C (see DTG curve, Fig. 1). Virtually the same thermal behaviour has been described earlier for the trifluoroacetates of some rare earth elements [6].

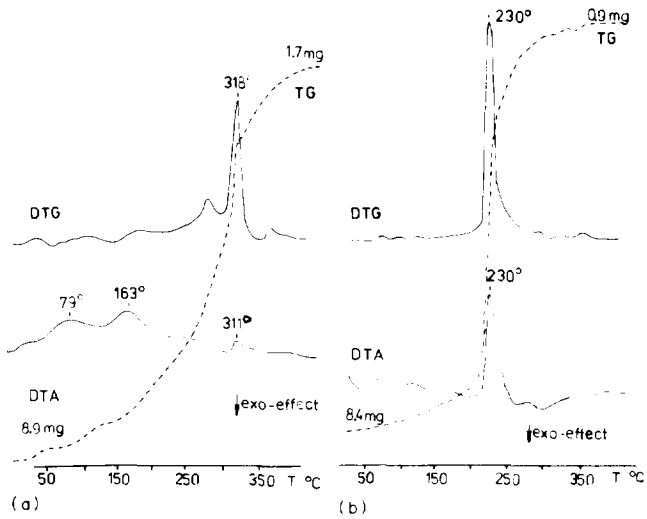

Fig. 1. Thermogravimetric curves for various $Cu(TFA)_2$ complexes. (a) Compound I; (b) compound II.

Dehydration is obviously accompanied by an increase in the coordinative unsaturation of the copper atom in compound I and may be the source of the instability of thin films of the sublimate of compound I. Indeed, we have observed that such films when deposited on silicon substrates decay completely in air within a few minutes. Such decay is accompanied by the rapid crystallization of the film and the formation of a dendrite-like structure. Hence ways of increasing the stability of the film become essential.

A possible solution to the problem may lie in the substitution of water in the crystalline solvate I by appropriate organic ligands. Attempts to synthesize TFA and related compounds in non-aqueous media have been described [7–9], but the discussion of the results obtained was generally limited by peculiarities in the behaviour of the substances in solution [7,8]. Data on the separation of the individual products are limited and somewhat contradictory [7,9]. The possible formation of complexes of $Cu(TFA)_2$ with methanol has been noticed; these were synthesized in 2,2-dimethoxypropane as a solvent with subsequent removal of water by azeotropic distillation [9], but the characteristics of the resulting complexes were not described. The most positive investigation has been of Cu(II) pentafluorobenzoate, which was shown to be capable of forming a stable 1:2 complex with 1,4-dioxan [10].

We have carried out the synthesis of $Cu(TFA)_2$ in a number of organic solvents (acetone, acetonitrile, tetrahydrofuran, etc.) by reaction of trifluoroacetic acid with copper(II) hydroxocarbonate, followed by the removal of the water formed by azeotropic distillation

with an excess of the solvent. Analysis of the experimental data obtained has shown 1,4-dioxan to be the optimal solvent and reagent for obtaining the most stable complexes. Thus, the synthesis of $Cu(TFA)_2$ in 1,4-dioxan leads to fine emerald green crystals of the 2:1 complex $2Cu(TFA)_2 \cdot C_4H_8O_2$ (compound II, Table 1).

In contrast to the analogous hydrate I, compound II is not at all hygroscopic and does not undergo any transformations, being stable in air for long periods of time. Thermogravimetrical data for this compound are presented in Fig. 1(b). The virtually smooth DTA curve at lower temperatures indicates the absence of thermal decomposition process under conditions which lead to the sublimation of I and the elemental analysis results indicate that the composition of the substance before and after sublimation is virtually unchanged (see Table 1). Thermal destruction of complex II occurs at 230 °C (DTG curve, Fig. 1(b)), but the vapour pressure of the compound at 140–150 °C is more than sufficient to obtain stable thin films by evaporation. These films can be maintained in air over a few days without any changes in their composition occurring.

To investigate the nature of the influence of fluorine atoms on the properties of compound II, the corresponding acetate [$CuAc_2$ (III)] and trichloroacetate [$Cu(TCA)_2$ (IV)] complexes were synthesized under the same conditions in 1,4-dioxan. It is interesting that the hydrocarbon compound III crystallizes from the hot solutions as a 1:1 complex, its perfluorinated analogue II as a 2:1 complex and its perchlorinated analogue IV as a 1:2 complex (see Table 1). Thus, the composition of the dioxan complexes obtained seems to be determined by the nature of the radical in the precursor acid.

Investigation of the volatility of the copper(II) alkylacetates obtained from aqueous solutions has shown their degree of sublimation does not exceed 4%–5% [11]. Nevertheless, the dioxan acetate complex III has turned out to be capable of sublimation but, as in the case of compound I, with decomposition. Thermogravimetric data for complexes III and IV are presented in Fig. 2. DTA and DTG curves show both compounds to be volatile but, in contrast to the perfluorinated analogue II, their sublimation is accompanied by the complete elimination of dioxan at temperatures below 100 °C. Elemental analysis data for the sublimates obtained in these cases show that they are the free anhydrous salts (see Table 1). Hence, the fluorine atoms in the complex increase the thermal stability of the dioxan complex of $Cu(TFA)_2$ relative to those of its non-fluorinated analogues. Thin films of anhydrous $CuAc_2$ and $Cu(TCA)_2$, obtained by thermal evaporation

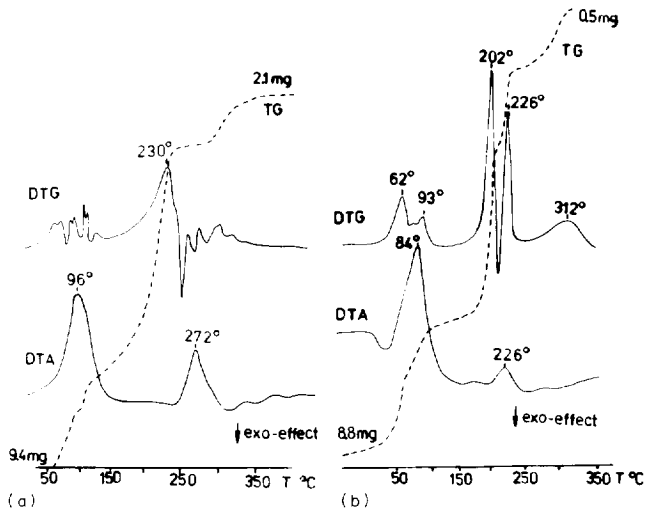

Fig. 2. Thermogravimetric curves for dioxan complexes of $Cu(TFA)_2$ analogues. (a) Compound III; (b) compound IV.

of complexes III and IV, respectively, have a reasonable stability.

Hence, the copper(II) TFA complex with 1,4-dioxan and its non-fluorinated analogues may be considered prospective and readily available precursors for obtaining stable copper-containing thin films via the MOCVD process.

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