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Thermal Behavior of the Heteroligand (μ_3-Fluoro)hexakis(μ_2-trifluoroacetato)tris(pyridine)tricobaltate(II) Tetramethylammonium Complex $(NMe_4)[Co_3F(TFA)_6(Py)_3]$

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Abstract—A new trinuclear triangular cobalt complex $(NMe_4)[Co_3(\mu_3F)(TFA)_6(Py)_3]$ (**I**) is synthesized by crystallization from a methanol solution. The crystal structure of complex **I** is solved by single-crystal X-ray diffraction analysis (CIF file CCDC no. 2151075). The Knudsen effusion method combined with mass spectral analysis of gaseous vaporization products shows that the heating of complex **I** under reduced pressure results in the removal of $(CH_3)_4NF$ as $(CH_3)_3N$ and CH_3F and of pyridine to form anhydrous cobalt trifluoroacetate $Co(CF_3COO)_2$, which sublimes on further heating to the monomer and dimer. The decomposition of $Co(CF_3COO)_2$ with the formation of CoF_2 and release of CO_2 and COF_2 occurs along with sublimation. Experiments on the iso- and polythermal vaporization makes it possible to calculate the partial pressures of the major gaseous products, to determine the standard enthalpies of sublimation of the monomer (137.9 ± 12.2 kJ/mol) and dimer (147.0 ± 21.6 kJ/mol) in a temperature range of 460–540 K, and to find the enthalpy of dissociation of the dimer (128.8 ± 25.8 kJ/mol). The study of the thermal stability of complex **I** in an argon flow (p = 1 atm) by gravimetry combined with mass spectral analysis of gaseous products confirms the three-stage decomposition of complex **I**. Unlike heating in vacuo, no sublimation of $Co(TFA)_2$ is observed under these conditions, and the decomposition of $Co(TFA)_2$ results in the formation of CoF_2 and is accompanied by the release of gaseous $(CH_3)_3N$, CH_3F, Py, CO, CO_2, CHF_3, CF_3COF, $(CF_3CO)_2O$, CF_3COCF_3, and C_2F_4. The presence of moisture and oxygen traces in argon leads to a decrease in the content of easily hydrolyzed products and formation of the oxidation and hydrolysis products: H_2O, HF, and CF_3COOH.

Keywords: cobalt compounds, thermodynamics, mass spectrometry, thermogravimetry

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INTRODUCTION

Trifluoroacetate complexes of transition metals demonstrate an interesting crystal structure forming isle structures containing coordination oligomers of diverse nuclearity or extended structures (coordination polymers). The synthesis and study of the crystal structures and magnetic behavior of such compounds are of significant interest [1]. The ability of the trifluoroacetate complexes to decompose with the formation of fluorides makes them convenient precursors for the preparation of fluoride materials [2–4]. Since interest in the fluoride-based materials is very high, importance of this application of trifluoroacetates can hardly be overrated. In particular, cobalt(II) fluoride is used to produce numerous functional materials and can be applied as a working body in diverse electronic devices. For instance, iron- or copper-doped CoF_2 is an efficient catalyst of water electrolysis aimed at generating hydrogen [5–7]. The presently used catalysts based on noble metals are not appropriate for large-scale production because of high cost and restricted resources. Nanosized fluorides of transition metals and, particularly, cobalt fluoride are used as cathodes in lithium-ion batteries due to good stability under normal conditions, high theoretical values of emf, good capacity, high charge transfer, etc. [8–10]. Cobalt fluoride is considered as a very promising material for using as a resist in electron-beam lithography to prepare magnetic nanostructures to 5 nm in size [11, 12].

In addition, cobalt difluoride can be a convenient precursor for the formation of oxide nanocrystalline or film working bodies in electronic sensors and indicators. The thermal decomposition and vaporization of polyvalent metal trifluoroacetates were shown [13–17] to be accompanied by the formation of fluorides that can transform into oxofluorides or oxides in an inert atmosphere containing oxygen in the amounts at most

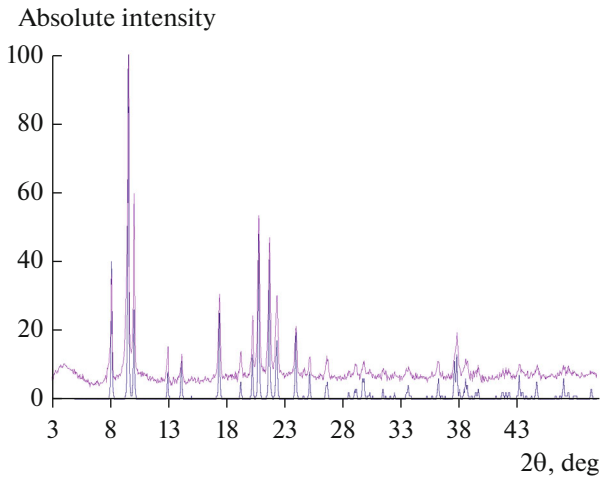

Fig. 1. XRD pattern of a polycrystalline sample of complex **I** (marked with violet) compared to the theoretical pattern (marked with blue).

0.01–2%. For example, the thermal decomposition of yttrium trifluoroacetate [18] in a temperature range of 200–250°C affords YF_3 that transforms into oxide in the presence of oxygen at $T > 1100$°C. The method for preparing a high-quality epitaxial superconducting film based on YBCO by the decomposition of the corresponding trifluoroacetates followed by the transition from fluorides to oxides due to pyrohydrolysis is also well-known [19].

Therefore, it seems rather promising to use trifluoroacetate coordination compounds of *d*-transition metals as universal precursors for the synthesis of fluoride, oxofluoride, and oxide nanomaterials, films, and coatings. The use of such precursors is prevented by instability of many trifluoroacetates in air because of their hygroscopicity. Therefore, the search for anhydrous trifluoroacetate complexes stable on storage in air is highly urgent. We have recently synthesized such a complex: (μ_3-fluoro)hexakis(μ_2-trifluoroacetato)tris(pyridine)tricobaltate(II) tetramethylammonium $(NMe_4)[Co_3F(TFA)_6(Py)_3]$ (**I**). This work is devoted to the study of the thermal stability and composition of the gas phase and determination of the thermodynamic characteristics of complex **I**.

EXPERIMENTAL

A 1.5 M solution (1.00 mL) of pyridine in methanol was added to a solution containing $CoTFA_2{\cdot}4H_2O$ (0.535 g, 1.5 mmol) and $Me_4NF{\cdot}4H_2O$ (0.0826 g, 0.5 mmol) in methanol (5 mL). The resulting solution was placed above phosphorus anhydride in a desiccator. Stable in air crimson platy crystals of complex **I** with a size of 2–4 mm were formed for a week due to the complete removal of the liquid phase. The composition and crystal structure of the prepared sample were determined by X-ray diffraction analysis (XRD) [20].

The single-phase character of the prepared sample was checked by powder XRD. The powder XRD pattern was measured on an EMPYREAN powder diffractometer (CuK_α radiation, voltage/current on the tube 45 kV/40 mA, reflection recording in the range 3°–50° 2θ with an increment of 0.033°, X'celerator linear solid-phase detector, continuous scan mode, and scan rate 1 deg/min). According to the obtained powder XRD pattern, the sample is single-phase: all lines correspond to the theoretical lines calculated from the XRD data (Fig. 1).

The thermal stability of complex **I** under atmospheric pressure was studied by thermogravimetric analysis (TG) synchronized with the mass spectral analysis of the formed gaseous products. TG analysis was carried out on heating a polycrystalline sample of compound **I** to 500°C at the rate from 0.2 to 10 K/min an argon flow (50 mL/min) using a NETZSCH STA 449 F3 Jupiter thermoanalyzer (NETZSCH, Selb, Germany). The gas phase composition was monitored on a QMS 403 Quadro quadrupole mass spectrometer (NETZSCH, Selb, Germany).

The vaporization of complex **I** was studied on an MS-1301 mass spectrometer designed for thermodynamic studies using a standard Knudsen molybdenum effusion cell with the ratio of the vaporization to effusion surface areas ≥600. The temperature was measured with a Pt-Pt/Rh thermocouple and maintained constant with an accuracy of ± 1 deg.

RESULTS AND DISCUSSION

According to the single-crystal XRD results, the crystal structure of complex **I** consists of tetramethylammonium cations and trinuclear complex anions $[Co_3(\mu_3\text{-}F)(TFA)_6Py_3]^-$ (TFA is trifluoroacetate, and Py is pyridine) formed by the cobalt(II) atoms that occupy vertices of a regular triangle and coordinate the μ_3-F atom arranged at the triangle center (Fig. 2). The Co atoms are linked in pairs by the bridging trifluoroacetate groups, and the octahedral coordination of cobalt is supplemented by the pyridine molecules occupying the axial vertices [20].

The TG study of the thermal stability of complex **I** under atmospheric pressure showed three stages on the mass loss curve at a heating rate of 5 K/min. The first decomposition stage starts at the temperature about 473 K with the corresponding endothermic effect (T_{max} = 536 K) (Fig. 3a). An inflection is observed at 542 K, and the mass loss in the first region (about 20%) corresponds to pyridine removal.

The second decomposition stage is observed in a temperature range of 543–568 K with the corresponding endothermic effect (T_{max} = 548 K), and the relative weight of the sample at the end of the second decomposition stage (71.4%) is close to the removal of

tetramethylammonium fluoride (m_{theor} = 72.12%) and formation of anhydrous cobalt trifluoroacetate.

The third decomposition stage occurs in a temperature range of 563–573 K with the corresponding exothermic effect at 568 K. The decomposition at this stage occurs with a high rate in the narrow temperature range (the sample loses 40% of mass in the region from 565.6 to 570.6 K). The weight of the final product (28.1%) somewhat exceeds the calculated weight of CoF_2 (24.4%), remains unchanged up to 606 K, and begins to decrease with further heating. This behavior of the sample can be explained by the fact that above a certain temperature the formed cobalt fluoride begins to interact with water vapors present in the carrier gas due to which oxide is formed resulting in the mass loss. The fact that the weight of the sample initially exceeds the calculated weight of cobalt difluoride is possibly due to the ability of the released fluorine-containing decomposition products, in particular, HF, to react, in part, with an alundum crucible, which results in some weighing of the crucible owing to the substitution of oxygen by fluorine.

Upon heating a sample of complex **I** with a rate of 0.2 K/min, the decomposition stages shifted to the range of lower temperatures and became more distinct (Fig. 3c). The inflection between the first and second decomposition stages became more distinct, and the corresponding plateau between the second and third stages appeared on the mass loss curve at the temperature from 523 to 553 K (Fig. 3b).

The mass spectrum of the gaseous decomposition products was decoded on the basis of the published data on the decomposition of trifluoroacetates [14, 21, 22] and reference data on the mass spectra of molecules obtained by the electron impact method [23]. According to the results obtained, the thermal decomposition of compound **I** is accompanied by the transition of Py, $(CH_3)_3N$, CH_3F, CO_2, CO, CHF_3, HF, and HTFA molecules to the gas phase. In addition, $(CF_3CO)_2O$, CF_3COCF_3, CF_3COF, C_2F_4, C_2F_6, and COF_2 are present in appreciable amounts, but the last two gases were detected not in all experiments. The obtained results confirm that argon used as the carrier gas contained a noticeable amount of water due to which the gas phase contained the hydrolysis products HF and HTFA. The presence of methyl fluoride and trimethylamine in the gas phase can be explained by the fact that the removal of the tetramethylammonium cation when heating complex **I** is similar to the decomposition of $(CH_3)_4NF$ with the formation of precisely these products [24].

The consequence of the appearance of ions corresponding to Py and CH_3F is consistent with the steps observed on the mass loss curve (Fig. 3d). After these gaseous products were removed, anhydrous cobalt trifluoroacetate is formed and decomposes, in turn, at the next stage. The gaseous products corresponding to this decomposition stage are consistent with the literature data. For example, CO, CO_2, CF_3CFO, CF_3H, C_2F_6 and $(CF_3CO)_2O$ were identified as the decomposition products of transition metal trifluoroacetates [21]. The anhydride is indicated as the major product of lanthanide trifluoroacetate decomposition in a dry atmosphere, and its decomposition gives COF_2 and CF_3COF [22]. Finally, C_2F_4 and CF_3COCF_3 molecules were observed upon the decomposition of alkaline metal trifluoroacetates [14]. The presence of water vapors results in hydrolysis reactions involving CF_3CFO, $(CF_3CO)_2O$, and COF_2 with the formation of CO_2, HF, and CF_3COOH, which is well consistent with published data [22].

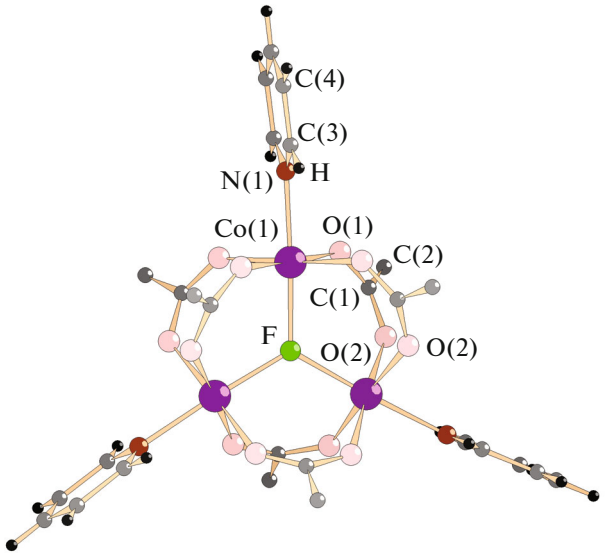

Fig. 2. Structure of the trinuclear $[Co_3(\mu_3\text{-}F)(TFA)_6Py_3]^-$ anion in the crystal structure of compound **I** (CF_3 groups are omitted for clarity).

The vaporization of cobalt complex **I** was studied in a temperature range of 320–570 K. The intensities of the base ions detected in the mass spectrum of the saturated vapor at different temperatures in the effusion chamber are given in Table 1.

An analysis of the experimental data and energy of ionization processes of the base ions presented in Table 1 suggests that the vaporization of complex **I** is accompanied by the successive transition to the gas phase of pyridine C_5H_5N molecules, monomer and dimer of cobalt trifluoroacetate $((CF_3COO)_2Co)_n$ (n = 1, 2), carbonyl fluoride (COF_2) molecules, and carbon oxides CO and CO_2. Our experimental data detected no transition to the gas phase of the thermolysis products of tetramethylammonium fluoride $(CH_3)_4NF$, which can be explained by different routes of the thermal dissociation of complex **I** under atmospheric pressure and in vacuo. Possibly, under the mass spectral experimental conditions, tetramethylammonium fluoride is detached at the temperature

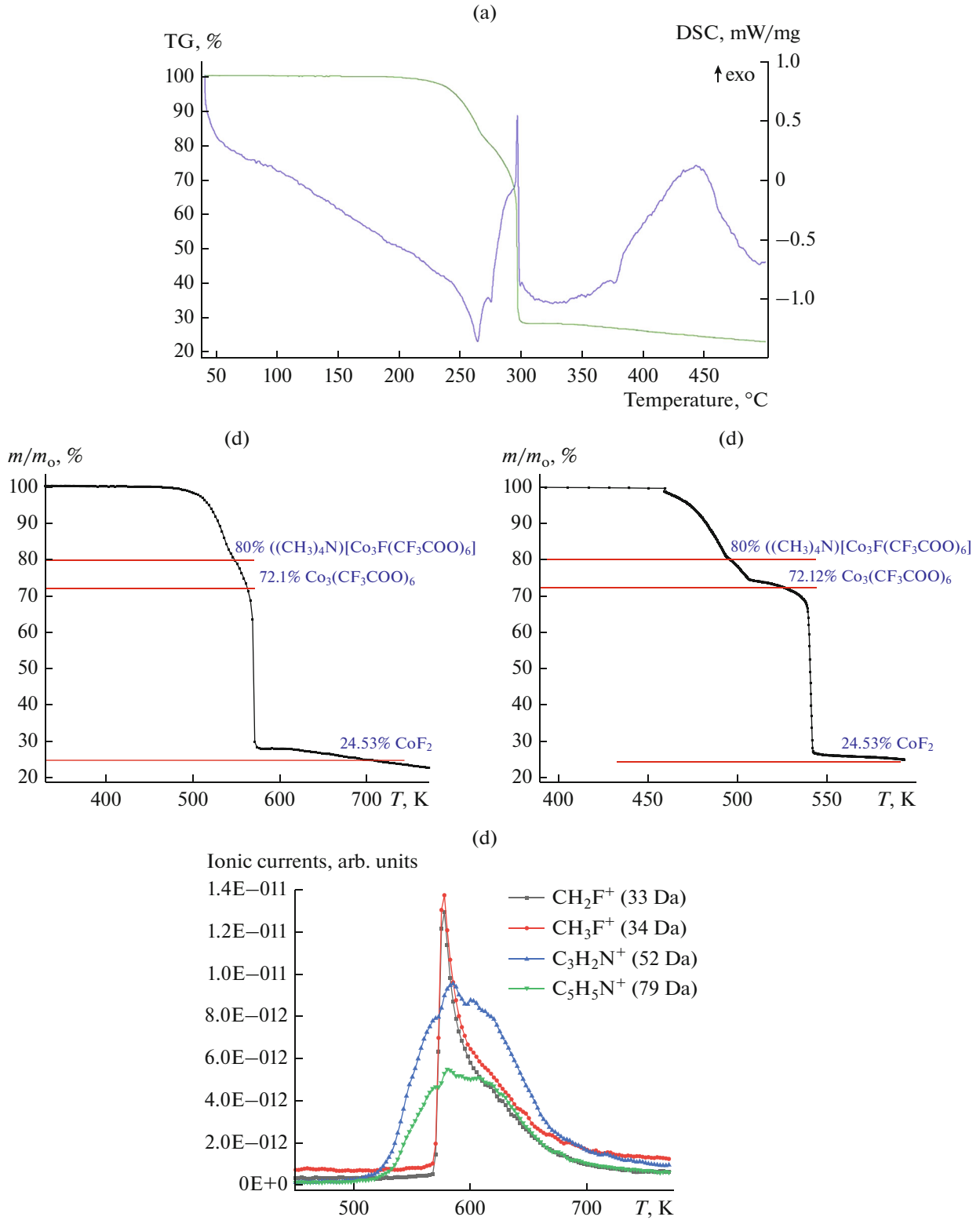

Fig. 3. TG analysis of complex **I**: (a) mass loss and DSC curves at a heating rate of 5 K/min, (b) mass loss curve at a heating rate of 5 K/min; (c) mass loss curve at a heating rate of 0.2 K/min; and (d) temperature dependences of the intensities of the base ions in the mass spectra of pyridine (52 and 79 Da) and fluoromethane (33 and 34 Da).

close to room temperature when the instrument is prepared for operation. It should be taken into account that a gate closing the effusion hole is used to detect molecules evolved from the effusion chamber. However, owing to the low condensation temperature (boiling points of $(CH_3)_3N$ and CH_3F are 275.7 and 194.8 K, respectively), both decomposition products can weakly react to the closure of the effusion hole and, hence, their identification becomes difficult.

To determine the character of vaporization and calculate the partial pressures, we carried out an experiment on the full vaporization of the known weighed sample of the complex at several constant temperatures. The experimental results are shown in Fig. 4. At T = 355 K, nearly constant ionic current intensities $I_{C_5H_5N^+}$ and $I_{C_3H_3N^+}$ primarily correspond to the transition of C_5H_5N pyridine molecules to the gas phase until their complete disappearance. The subsequent constant ionic current intensities I_{CoO^+}, $I_{CF_3^+}$, $I_{CoFCF_3COO^+}$, and $I_{Co_2(CF_3COO)_3\text{-}F^+}$ at T = 530 K up to their complete disappearance reflect the transition to the gas phase of cobalt trifluoroacetate and carbon carbonyl fluoride molecules.

According to the XRD data, cobalt difluoride remained in the effusion chamber after the end of sublimation of the cobalt complex. The dark brown color of cobalt difluoride indicates, most likely, the presence of carbon as an impurity in its composition. Taking into account the aforesaid, the vaporization of the cobalt compound under reduced pressure can be presented as three stages by the following reactions (hereinafter, the products for which the phase individuality was not confirmed are in quotes, and subscripts g and s imply the gas and solid states, respectively):

1 stage T = 290–320 K

$$NMe_4[Co_3F(TFA)_6(Py)_3]_s = 3\text{“}(Co(TFA)_2(Py))_s\text{”} + Me_3N_g + MeF_g \quad (1)$$

2 stage T = 340–430 K

$$\text{“}Co(TFA)_2(Py)_s\text{”} = Co(TFA)_{2s} + Py_g \quad (2)$$

3 stage T = 460–540 K

$$Co(TFA)_{2s} = Co(TFA)_{2g}, \quad (3)$$

$$2Co(TFA)_{2s} = [Co(TFA)_2]_{2g}, \quad (4)$$

$$Co(TFA)_{2s} = CoF_{2s} + 2CF_2O_g + 2CO_g. \quad (5)$$

Experiments on the full vaporization of the cobalt complex and knowledge of all vaporization reactions (1)–(5) forming gaseous and solid components made it possible to use the Hertz–Knudsen equation written for the second and third vaporization stages

$$q_{Py} = S_{eff}k_{Py}\left(\frac{TM_{Py}}{2\pi R}\right)^{1/2}\int_0^{t_1} I_{Py}dt,$$

Table 1. Mass spectra of the gas phase of the cobalt complex at 350 and 525 K

m/z	Ion	Intensity, %
	T = 350 K	
52	$C_3H_2N^+$	85
79	$C_5H_5N^+$	100
	T = 525 K	
69	CF_3^+	24
47	COF^+	22
66	COF_2^+	12
75	CoO^+	100
250	$CoFCF_3COO^+$	4
394	$Co_2(CF_3COO)_2^+$	4
438	$Co_2(CF_3COO)_3\text{-}F^+$	4
28*	CO^+	5×10^4
44*	CO_2^+	10^4

* The total intensities of ionic currents with m/z = 28 and 44 are presented.

$$q_{Co(TFA)2} = S_{eff}k_{Co(TFA)2}\left(\frac{TM_{Co(TFA)2}}{2\pi R}\right)^{1/2}\int_{t1}^{t_2} I_{Co(TFA)2}dt,$$

$$q_{CF2O} = S_{eff}k_{CF2O}\left(\frac{TM_{CF2O}}{2\pi R}\right)^{1/2}\int_{t_1}^{t_2} I_{CF2O}dt$$

(where $q_{py}(q_{Co(TFA)2}, q_{CF2O})$ is the weighed sample evaporated as pyridine (cobalt trifluoroacetate, car-

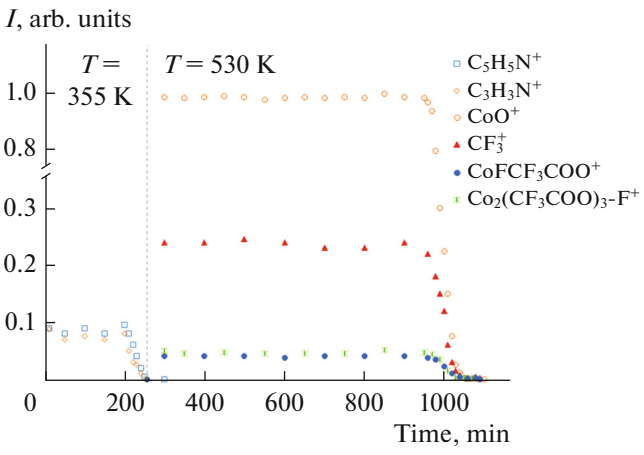

Fig. 4. Isotherm of the full sublimation of a weighed sample of cobalt: □, $I_{C_5H_5N^+}$; ◇, $I_{C_3H_3N^+}$; ○, I_{CoO^+}, ▲, $I_{CF_3^+}$; ●, $I_{CoFCF_3COO^+}$; and ✳, $I_{Co_2(CF_3COO)_3\text{-}F^+}$.

Table 2. Partial pressures (Pa) of the components of the gas phase above the cobalt(II) trifluoroacetate complex

Phase	Partial pressures					T, K
	C_5H_5N	$Co(TFA)_2$	$[Co(TFA)_2]_2$	CF_2O	CO*	
$Co(TFA)_2 \cdot 3Py$	4.3×10^{-3}	–	–	–	–	358
	1.2×10^{-1}	–	–	–	–	413
$Co(TFA)_2$	–	6.3×10^{-2}	3.7×10^{-3}	6.0×10^{-2}	3.9×10^{-2}	504
	–	1.2×10^{-1}	6.9×10^{-3}	1.1×10^{-1}	7.2×10^{-2}	513

* Calculated from the equality of the molecular flows of CF_2O and CO molecules leaving the effusion chamber.

Table 3. Enthalpies (kJ/mol) of reactions (2)–(4)

Reaction 2 340–430 K		Reaction 3 460–540 K		Reaction 4 460–540 K
$C_5H_5N^+$	$C_3H_5N^+$	CoO^+	CF_3^+	$[Co_2(CF_3COO)_3\text{-}F]^+$
123.1 ± 4.4	118.5 ± 7.6	152.5 ± 11.8	148.7 ± 12.3	142.2 ± 15.9
125.6 ± 5.8	119.8 ± 12.2	126.1 ± 13.1	141.5 ± 11.0	166.7 ± 4.6
111.4 ± 5.8	–	134.9 ± 5.8	131.6 ± 9.70	137.0 ± 7.8
114.3 ± 3.2	–		138.1 ± 7.7	131.5 ± 16.9
122.6 ± 5.7	–	129.1 ± 9.3	–	160.5 ± 7.2
125.5 ± 18.5	–	–	–	144.2 ± 6.4
120.4 ± 12.8	119.2 ± 13.2	135.7 ± 11.8	140.0 ± 17.5	147.0 ± 21.6

bonyl fluoride), S_{eff} is the effective effusion surface area, k_j is the constant of instrument sensitivity for the jth component, T is temperature, R is the universal gas constant, M_j is the molar weight of the jth component of the gas phase, t is the sublimation time, and I_j is the total ionic current formed by the ionization of the jth component of the gas phase) and the main equation of mass spectroscopy $p_j = k_j I_j T$ (k_j is the sensitivity coefficient with respect to molecules j) for the calculation of the absolute partial pressures p_j at the last two sublimation stages of the complex under study (Table 2).

The enthalpies of reactions (2)–(4) were calculated from the ionic current intensities $I_{C_5H_5N^+}$, $I_{C_3H_3N^+}$, I_{CoO^+}, $I_{CF_3^+}$, and $I_{Co_2(CF_3COO)_3\text{-}F^+}$ in the temperature ranges 340–430 and 460–540 K by least squares using the van't Hoff and Clausius–Clapeyron equations. The enthalpies of these reactions obtained for different ions and consistent with each other are given in Table 3. This result can be considered as a confirmation of the valid determination of the composition of the gas phase above cobalt trifluoroacetate.

The following enthalpies of reactions (2), (3), and (4) were accepted on the basis of the results listed in Table 3: ΔH_T° (2) = 119.0 ± 11.5, ΔH_T° (3) = 137.9 ± 12.2, and ΔH_T° (4) = 147.0 ± 21.6 kJ/mol.

The enthalpy of dissociation was calculated from the known enthalpies of sublimation of dimeric and monomeric cobalt trifluoroacetate molecules

$$[Co(TFA)_2]_{2g} = 2Co(TFA)_{2g}, \quad (6)$$

which turned out to be ΔH_T° (6) = 128.8 ± 25.8 kJ/mol. Based on the obtained value and partial pressures of the monomer and dimer (Table 2), we estimated the entropy of dissociation as ΔS_T° (6) = 159.3 ± 26 J K^{-1} mol^{-1} (38.1 eu).

The thermodynamic characteristics of the coordination cobalt(II) compounds based on trifluoroacetic acid determined in this work can be used for the synthesis of CoF_2 as both the crystalline phase formed by the decomposition of compound **I** under atmospheric pressure (reactions (1), (2), and (5)) as thin films or coatings prepared using the CVD procedure under reduced pressure (reactions (1)–(4)) by the decomposition of the $Co(TFA)_2$ film (reaction (5)) immobilized on the support at elevated temperatures. The obtained value of ΔS_T° (6) can further be used for choosing an optimum model of the monomer and dimer structure in the gas phase by comparing with the theoretically calculated entropy.

Thus, the study of the behavior of trifluoroacetate complex **I** on heating showed that the complex can be used as a stable (on storage in air) precursor for the

preparation of cobalt fluoride as crystalline samples or thin films.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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