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Binary Complexes $[Co(A)_6][M(C_2O_4)_3]$ ($A = NH_3$, $1/2C_2H_8N_2$, M = Fe, Cr): Synthesis, Properties, and Thermal Decomposition

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Abstract—Binary complexes $[Co(A)_6][M(C_2O_4)_3]$ ($A = NH_3$, $1/2C_2H_8N_2$, M = Fe, Cr) are synthesized, and their physicochemical properties and thermal decomposition in air, argon, and hydrogen are studied. The qualitative and quantitative analyses are carried out for the solid and gaseous thermolysis products. Similar regularities are revealed in the behavior of complexes $[Co(NH_3)_6][Fe(C_2O_4)_3]$ (**I**), $[Co(En)_3][Fe(C_2O_4)_3]$ (**II**), $[Co(NH_3)_6][Cr(C_2O_4)_3]$ (**III**), and $[Co(En)_3][Cr(C_2O_4)_3]$(**IV**). The solid thermolysis product for complexes **I** and **III** in argon at 225 and 300°C is $Co(NH_2)_2M(C_2O_4)_2$, respectively; and that for complexes **II** and **IV** at 280 and 380°C is $Co(En)_2M(C_2O_4)_2$. The gaseous thermolysis products are CO and CO_2, NH_3, En partially isolated upon thermal destruction, other products of En destruction, and En itself. Complex **III** forms the most highly dispersed solid products in a range of 300–400°C.

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INTRODUCTION

In order to study possibilities for the preparation of highly dispersed bimetallic powders by the thermal decomposition of complexes, we studied the syntheses and thermolyses of binary complexes $[M^IA_6]_x[M^{II}(CN)_6]_y \cdot nH_2O$ (M^I = Co (Co(III), Ni(II), Cr(III), Cu(II); M^{II} = Fe(III), Fe(II), Cr(III), Co(III); A = NH_3, 1/2En ($C_2H_8N_2$), 1/2Pn ($C_3H_{10}N_2$), urea) [1–6]. The compositions and crystalline modifications of the compounds were studied. Thermolysis was carried out in air, hydrogen, and argon. The compositions of the solid and gaseous thermolysis products were studied. In a reductive atmosphere coordinated cyano groups undergo complete or partial hydrogenation [7], and the metals, except for chromium, are reduced to form intermetallic compounds [1–3, 5]. Ammonia is isolated in the unchanged state, and other ligands of the cationic part of the binary complexes are partially isolated in the unchanged state, as destruction products and partially decompose in the solid phase to carbon. Hydrogen cyanide is also isolated in an inert atmosphere, whereas hydrogen cyanide, water, CO, and CO_2 are formed in an oxidative atmosphere. The solid thermolysis products in the oxidative medium are oxides of central atoms, and multiphase products are formed in an inert medium. The multiphase products contain oxides, intermetallic compounds, individual metals, metal carbides and nitrides, and mainly large amounts of residual carbon as an individual amorphous phase (up to 65% of the initial carbon content). A significant amount of ammonia is formed in all atmospheres as a destruction product of amines and urea [1–6]. Thus, the course of thermolysis of the binary complexes containing the $[M(CN)_6]^{n-}$ anion is determined by the nature of the thermolysis atmosphere and is complicated.

For this reason, it is of interest to study the thermolysis of binary complexes containing no cyanides. We also studied the thermolysis of the binary complex with the $[Cr(CNS)_6]^{3-}$ anion [8]; however, it turned out that the presence of sulfur in the anion impeded the reduction of metals and made this process more difficult.

This work is devoted to the study of binary complexes $[Co(A)_6][M(C_2O_4)_3] \cdot nH_2O$ ($A = NH_3$, M = Fe (**I**); A = En, M = Fe (**II**); $A = NH_3$, M = Cr (**III**); A = En, M = Cr (**IV**)). These binary complexes contain no cyano groups forming bridges, and their example makes it possible to easily monitor the influence of the replacement of ligands in the cation on the thermolysis process and the properties of its products and to identify almost all gaseous thermolysis products. As mentioned [9], the oxalate complexes have many advantages over other complexes: they provide a high purity of the thermolysis products and make it possible to obtain oxides with specified properties.

EXPERIMENTAL

The binary complexes were prepared by mixing aqueous solutions of equivalent amounts of the cationic and anionic complexes $[Co(NH_3)_6]Cl_3$, $[Co(En)_3]Cl_3$, $K_3[Fe(C_2O_4)_3]$, and $K_3[Cr(C_2O_4)_3]$ synthesized according to the manual [10]. The following

Table 1. Elemental analyses results for compounds **I**–**IV**

Compound (empirical formula, FW)	Content (found/calculated), %		
	Co	Fe (Cr)	C
[Co(NH$_3$)$_6$][Fe(C$_2$O$_4$)$_3$] · 2H$_2$O (**I**) (C$_6$H$_{22}$N$_6$O$_{14}$CoFe, 516.77)	11.8/11.4	10.3/10.8	14.4/13.9
[Co(En)$_3$][Fe(C$_2$O$_4$)$_3$] · 2H$_2$O (**II**) (C$_{12}$H$_{28}$N$_6$O$_{14}$CoFe, 594.77)	9.9/9.9	9.2/9.4	25.1/24.2
[Co(NH$_3$)$_6$][Cr(C$_2$O$_4$)$_3$] · 3H$_2$O (**III**) (C$_6$H$_{24}$N$_6$O$_{15}$CoCr, 530.93)	10.1/11.1	10.2/9.8	13.7/13.6
[Co(En)$_3$][Cr(C$_2$O$_4$)$_3$] · 4H$_2$O (**IV**) (C$_{12}$H$_{32}$N$_6$O$_{16}$CoCr, 626.93)	9.2/9.4	8.6/8.3	22.1/22.9

reagents (all reagent grade) were used in the syntheses: CoCl$_2$ · 6H$_2$O, FeCl$_3$, K$_2$Cr$_2$O$_7$, K$_2$C$_2$O$_4$ · H$_2$O, oxalic acid, KOH, KHCO$_3$, a concentrated solution of ammonia, and a 70% solution of ethylenediamine.

The compounds were identified by chemical analysis and IR spectroscopy. Analyses to metals were carried out on an AAnalyst 400 spectrometer in solutions of the binary compounds in a mixture of hydrochloric and nitric acids. Analysis to carbon was carried out on an ELTRA CS-2000 automated analyzer. The elemental analyses results for the binary complexes are presented in Table 1.

Diffraction patterns were measured on a Shimadzu XRD 6000 diffractometer (CuK_α radiation, graphite monochromator). The most intense reflections with interplanar distances (*d*/*n*, nm/*I*) are as follows: for **I**, 0.88/100, 0.44/99, 0.45/93, 0.53/92, 0.41/55, 0.33/51, 0.29/49, 0.46/46, and 0.34/43; for **II**, 0.65/100, 0.46/60, 0.33/47, 0.38/37, 0.23/35, and 0.47/15; for **III**, 0.47/100, 0.62/55, 0.26/36, 0.36/23, 0.32/22, and 0.37/20; and for **IV**, 1.15/100, 0.38/37, 0.56/23, 0.30/13, and 0.76/11.

IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer in a range of 4000–400 cm^{-1} in KBr pellets. The published source [11] was used for the identification of the binary complexes by IR spectroscopy.

IR, ν, cm^{-1}: for **I** 3555, 3452 ν(OH); 3296, 3203 ν(NH); 1708, 1659 ν_{as}(C=O); 1413 ν_s(C–O) + ν(C–C); 1284, 890, 861 ν_s(C–O) + δ(O–C=O); 799 ρ(OH$_2$); 535 ν(M–O) + ν(C–C); 487 δ_{cycle} + δ(O–C=O); for **II**, 3513 ν(OH); 3293, 3243, 3119 ν(NH); 2897 ν(CH); 2360 1705, 1688, 1660 ν_{as}(C=O); 1610 δ(OH$_2$); 1462 δ(CH$_2$); 1378 ρ_w(CH$_2$); 1244, 1230, 1152 ρ_w(NH$_2$); 1056 ν(C–C); 1006 ρ_t(NH$_2$); 879 ρ_c(CH$_2$); 797 ρ(OH$_2$); 529 ν(M–O) + ν(C–C); 486 δ_{cycle} + δ(O–C=O); for **III**, 3559, 3452ν (OH); 3304, 3195 ν(NH); 2925 ν(CH); 1708, 1682 ν_{as}(C=O); 1385 ν_s(C–O) + ν(C–C); 1254, 896 ν_s(C–O) + δ(O–C=O); 810 ρ(OH$_2$); 543 ν(M–O) + ν(C–C); 481 δ_{cycle} + δ(O–C=O); 414 ν(M–O) + δ_{cycle}; for **IV**, 3478 ν(OH); 3243, 3143, 2966 ν(NH); 2901 ν(CH); 1413 ν_s(C–O) + ν(C–C); 1708, 1686, 1650 ν_{as}(C=O); 1464 δ(CH$_2$); 1385 ρ_w(CH$_2$); 1252, 1153 ρ_w(NH$_2$); 1055 ν(C–C); 1008 ρ_t(NH$_2$); 892 ρ_c(CH$_2$); 853; 808 ρ(OH$_2$); 543 ν(M–O) + ν(C–C); 474 δ_{cycle} + δ(O–C=O); 417 ν(M–O) + δ_{cycle}.

Heterogeneity of the compounds was confirmed by crystal optic analysis using a Leica DM 2500 microscope and a standard set of immersion liquids. The following refraction indices were obtained: for **I**, dendrite-like crystals, $N'_p = 1.58$, $N'_g = 1.66$; for **II**, needle-like crystals, $N'_p = 1.59$, $N'_g = 1.70$; for **III**, needle-like fibrous crystals, $N'_p = 1.60$, $N'_g = 1.64$; and for **IV**, needle-like crystals, $N'_p = 1.60$, $N'_g = 1.64$. Compounds **I** and **II** are pale yellow, and compounds **III** and **IV** are greenish-gray.

Weighed samples of the binary compounds were dried to a constant weight at 110°C, the diffraction patterns were detected for the dried samples, and analyses to carbon were carried out. The mass losses during drying were the following: for **I**, 3.48; for **II**, 6.00; for **III**, 6.78; and for **IV**, 6.09%. It was shown that compounds **I** and **III** lost one water molecule each upon drying; compounds **II** and **IV** lost two molecules each, due to which compound **II** became anhydrous; and compound **IV** retained two water molecules. The loss of water for compounds **III** and **IV** is accompanied by a change in the color to light red and light green, respectively. The analyses to C in the dried samples are close to the calculated results. Found (%): 14.53 (**I**), 25.11 (**II**), 14.60 (**III**), and 24.89 (**IV**). Calculated (%): 14.97 (**I**), 25.77 (**II**), 14.55 (**III**), and 24.37 (**IV**).

The most intense reflections with interplanar distances (*d*/*n*, nm)/*I*) are the following: for **I**, 0.88/100, 0.55/92, 0.46/93, 0.44/99, 0.41/55, 0.33/51, 0.29/71, and 0.25/32; for **II**, 0.30/100, 0.34/74, 0.61/68, 0.39/43, and 0.58/38; for **III**, 0.62/55, 0.47/100, 0.26/36, and 0.36/23; for **IV**, 1.15/100, 0.56/23, 0.38/37, and 0.30/13.

Thermal analyses in air and argon were carried out on a NETZSCH STA 409 PC/PG instrument in a capped corundum crucible with a weighed sample of 6–10 mg and a heating rate of 10 deg/min. The thermograms (TG) of complexes **I** and **IV** are presented in Figs. 1 and 2. The compositions of the gaseous prod-

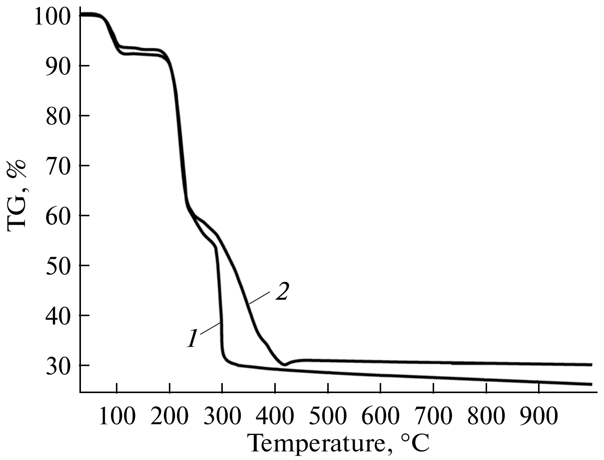

Fig. 1. TG curves for complex $[Co(NH_3)_6][Fe(C_2O_4)_3]$ in (*1*) air and (*2*) argon.

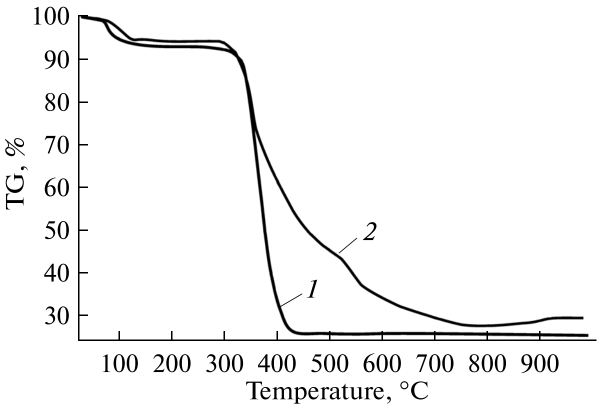

Fig. 2. TG curves for complex $[Co(En)_3][Cr(C_2O_4)_3]$ in (*1*) air and (*2*) argon.

ucts were also studied using a MAG gas analyzer (OOO Monitoring, St. Petersburg). The instrument determines the content of CO and CO_2 and volatile organics recalculated to methane in the gas flow. For an experiment, a weighed sample of a binary complex (0.2–0.4 g) was loaded into a quartz boat, which was placed in a flow-type tubular quartz reactor incorporated into a Nabertherm RT 50-250/11 tubular furnace. The heating rate of the furnace was 10 deg/min, and the gas flow rate was 1 L/min. The yield of the components of the gas flow in % of the total carbon content was determined from the surface area of the elution curves in the coordinates *c* (mol/L) vs. *V* (L) (Table 2). The surface area of the curves was calculated using the MATHCAD-15 program. The relative determination error was 5%.

Point experiments were made for the binary complexes. Weighed samples of the binary complexes were kept at a certain temperature for 1 h in a flow of air, hydrogen, or argon in the above mentioned quartz tubular reactor and cooled in the same atmosphere. Solid thermolysis products were analyzed to metal and carbon and subjected to X-ray diffraction analysis. For a hydrogen atmosphere, this is the single possible way for studying thermolysis. Crystalline products were identified according to [12]. Gaseous thermolysis products were trapped passing the outlet gas flow consequently through Drexel's bottles with titrated solutions of HCl and NaOH. The amounts of isolated ammonia and CO_2 were determined in these solutions by titration using two indicators [13]. The results of point experiments are presented in Tables 2–5.

Table 2. Results of quantitative gas analyses during the thermolysis of binary complexes **I**–**IV**

Binary complex	Weight, (mol × 10^3)	*c*, g-atom × 10^3	Co, mol × 10^4 (temperature range, °C)			Σ CO, %	CO_2, mol × 10^4 (temperature range, °C)			Σ CO_2, %
					In air					
I	0.4303 (0.833)	5.00	0.5 (325–340)			~1	17.25 (240–310)	33.1 (325–340)		96.7
II	0.3004 (0.581)	6.97	2.38 (305–334)			3.4	67.9 (302–350)			97.4
III	0.3415 (0.643)	3.86	3.92 (350–370)			9.8	5.2 (280–345)	30.7 (354–370)		93.0
IV	0.5302 (0.846)	10.15	5.0 (380–425)			5.0	77.1 (375–435)			75.9
					In argon					
I	0.3218 (0.623)	3.74	5.13 (350–445)			13.6	10.90 (240–310)	0.75 (340–370)	18.27 (370–470)	80.0
II	0.3388 (0.570)	6.84	28.0 (370–600)			40.9	2.33 (315–355)	12.5 (375–530)		21.7
III	0.4834 (0.910)	5.46	13.1 (325–420)	4.9 (420–540)		33.0	8.7 (255–345)	21.1 (345–415)		54.6
IV	0.4571 (0.729)	8.75	9.8 (370–475)	9.7 (475–590)	11.0 (590–800)	34.9	20.0 (368–526)			22.9

Table 3. Results of the point experiments in air

Binary complex	Temperature, °C	Solid products					Gaseous products (% of initial)	
		empirical composition	phase composition	Co	Fe (Cr)	C	CO_2	NH_3
I	270	$CoFeO_{4.3}$	$CoCo_2O_4$, Fe_3O_4, $CoFe_2O_4$	32.2	29.9	0.2	70	84
II	280	$CoFeC_{0.1}O_{3.4}$	$CoCo_2O_4$, $CoFe_2O_4$	34.6	32.6	0.7	82	28
III	310	$CoCrO_{4.7}$	Co_3O_4, $CoCr_2O_4$	31.3	28.7	Not found	62	61
IV	430	$CoCrO_{3.7}$	Co_3O_4, $CoCr_2O_4$	34.2	31.1	Not found	93	31

Table 4. Results of the point experiments in argon

Binary complex	Temperature, °C	Solid products					Gaseous products (% of initial)	
		empirical composition	phase composition	Co	Fe(Cr)	C	CO_2	NH_3
I	225	$C_4H_6N_2O_8CoFe$	Amorphous to X-ray	18.3	17.3	13.9	35	57
	425	$CoFeO_{2.4}$	CoFe, Fe_3O_4, $CoFe_2O_4$	38.3	33.8	0.1	80	86
II	280	*$C_{8.5}H_{16}N_4O_{10}CoFe$	Initial structure	13.2	12.4	21.2	26	Not found
	480	$CoFeC_{2.3}O_{3.5}$	CoFe, Fe	29.8	27.8	13.8	45	17
	600	$CoFeC_{2.3}O_2$	CoFe, Fe	34.2	30.5	15.8	46	12
III	300	$C_4H_6N_2O_8CoCr$	Amorphous to X-ray	17.4	15.4	14.1	20	66
	350	$CoCrC_3O_9$	Amorphous to X-ray	19.7	18.6	12.0	28	82
	380	$CoCrC_{0.7}O_4$	Amorphous to X-ray	31.1	27.2	4.2	38	96
IV	380	$C_8H_{16}N_4O_9CoCr$	Amorphous to X-ray	13.7	13.9	24.4	27	Not found
	600	$CoCrC_{2.5}O_4$	Co_3O_4, CrC_2O_4	28.9	25.6	14.5	26	31
	800	$CoCrC_{2.25}O_{3.5}$	Co_3O_4, CrC_2O_4	30.5	26.4	13.8	38	20

* Found, %: N—12.4; C—22.6; H—4.0; calculated, %: N—12.4 ; C—2.6; H—4.0.

RESULTS AND DISCUSSION

The samples retain the crystal structure due to drying to a constant weight, and a set of characteristic reflections of the dried sample differs from the corresponding set for the initial compound only for complex **II**. The structure of complex **IV** including long chains of alternating cations and anions oriented along the crystallographic axis *c* was found [9]. The ions are bound by multiply repeated hydrogen bonds N—H···O, and the N—H groups are linked to two different oxalate chelate rings. The adjacent chains are connected by strong hydrogen bonds. Probably, complexes **I**–**III** have similar structures. The ability of compounds **I**, **III**, and **IV** to retain some water of crystallization at 110°C also indicates the presence of strong hydrogen bonds.

Table 5. Results of the point experiments in hydrogen

Binary complex	Temperature, °C	Solid products					Gaseous products (% of initial)	
		empirical composition	phase composition	Co	Fe(Cr)	C	CO_2	NH_3
I	275	$C_3H_6N_2O_6CoFe$	Amorphous to X-ray	20.7	18.8	12.9	20	92
	400	$CoFeC_{0.2}O_{0.6}$	Fe, CoFe	46.6	42.3	1.7	83	81
	500	CoFe	CoFe	50.6	46.4	0.1	64	95
II	280	*$C_{8.5}H_{18}N_4O_{10}CoFe$	Initial structure	13.1	12.4	21.6	23	Not found
	480	CoFeCO	Fe, CoFe	41.8	40.2	8.1	35	29
	600	$CoFeO_{0.5}$	Fe, CoFe	47.7	44.9	0.0	58	50
III	275	$C_5H_6N_2O_{12}CoCr$	Amorphous to X-ray	14.2	13.2	15.0	41	56
	525	$C_{0.2}O_{3.8}CoCr$	$CoCr_2O_4$		30.8	1.3	60	92
IV	380	$C_{6.7}H_8N_2O_{7.5}CoCr$	Amorphous to X-ray	17.2	15.6	23.2	27	Not found
	600	$O_{2.5}CoCr$	CoO, Cr_2O_3	39.4	34.3	0.6	40	71

* Found, %: N—12.2; C—22.0; H—3.9.

The influence of the weight of the initial complex and the time of storage at the final temperature in the point experiments should be taken into account when analyzing the data on thermolysis. Compounds **I–IV** behave similarly during thermolysis in air. Coordinated water is removed in the range from 50 to 120–130°C, and then the ligands of the cation are eliminated followed by the stepped elimination of oxalate. According to the thermogram, after the water loss compound **I** retains a constant composition to ~190°C (Fig. 1), then compound **I** loses ammonia and approximately one $C_2O_4^{2-}$ group in a range of 210–240°C, and the remained oxalate is lost below 300°C. The residue after calcination is 30.49%, which is close to the composition CoO + $1/2Fe_2O_3$ (29.51%). According to the quantitative analysis results, two regions of CO_2 isolation are observed: 34.5% (240–310°C), which corresponds to the elimination of one oxalate group, and the rest carbon (320–340°C). An insignificant amount of CO (~1% of the total C content) is formed in the latter range (Table 2). In the point experiment at 270°C and storage for 1 h, the residue after calcination contains 0.2% C, and 70% of all carbon were found in the absorptive acidic solution (Table 3). A comparison of the point experiment result with the thermogram shows that the range of CO_2 isolation somewhat shifts to higher temperatures at the same heating rate for a larger weighed sample of the binary complex. The prolong storage results in the isolation of a larger amount of carbon. This complex decomposes most easily. According to the X-ray diffraction data, a $Fe_3O_4 + CoCo_2O_4 + CoFe_2O_4$ mixture is the thermolysis product of complex **I** in the point experiments in air at 270 and 400°C.

Binary complex **II** decomposes in air to the same product as complex **I** already at 340°C retaining a constant composition after water loss in a range of 100–230°C. The loss of ethylenediamine and oxalate occurs in one stage. The residue after calcination at 350°C is 29%, 1.5% are burned out below 500°C, and the calculated value for the CoO + $1/2Fe_2O_3$ mixture is 26.02%. An analysis of the gas phase confirms that almost all carbon is burned out in the range 300–350°C in the form of CO_2 (Table 2). The point experiment shows that nearly all carbon is removed due to the storage for 1 h (Table 3).

The thermolysis of complex **III** in air is similar to that for complex **I**: according to the thermogram, $\sim 1/2C_2O_4^{2-}$ is removed along with ammonia below 320°C, and the remained oxalate is eliminated below 370°C. The residue after calcination is 31.6%, which is close to CoO + $1/2Cr_2O_3$ (28.43%) or $CoCrO_3$ (29.93%). According to the X-ray diffraction data, a $CoCo_2O_4 + CoCr_2O_4$ mixture is the thermolysis product of complex **III** in air in the point experiments at 310 and 425°C. An analysis of the gas phase shows that 13.5% of the possible amount of CO_2 ($\sim 1/3C_2O_4^{2-}$) are isolated in the range 280–350°C, and 79% CO_2 and ~9% CO are formed in a range of 350–370°C (Table 2). The residue after calcination without carbon was obtained in the point experiment at 310°C (Table 3). Compound **IV** turned out to be most thermostable, retained a constant composition after drying in a range of 120–300°C, and then decomposed, as binary complex **II**, in one stage below 425°C to form a mixture of oxides. The residue after calcination at 425°C is 26%, and the calculated value for CoO + $1/2Cr_2O_3$ is 25.54% (Fig. 2). In the same range of 370–430°C 76% CO_2 and 5% CO are evolved. In addition, a fairly significant amount of undecomposed En is formed. The absorptive solution of the acid contains 90% CO_2 in the point experiment at 430°C, and no carbon was found in the solid residue (Table 3).

Somewhat overestimated content of oxygen in the calcination residues is an abundant phenomenon for thermolysis in air [1–7]. Possibly, oxygen is absorbed by the products or has no time to diffuse from crystals of oxides. Somewhat underestimated contents of ammonia and CO_2 were found in the gaseous thermolysis products of the ammonia complexes, but ammonium carbonate is deposited in the cold end of the reactor tube. For the thermolysis of the En-containing complexes, about 30% nitrogen present in the binary complex are evolved as ammonia.

The TG curves for compounds **I** and **III** in argon are also similar, although the temperature range of the reaction for complex **I** is by 100°C narrower than that for compound **III** (Fig. 1). According to the thermogram, complex **I** loses water of crystallization below 110°C and the dehydrated complex does not change the composition to 180°C, all ammonia is eliminated and about one oxalate group is removed in the range from 180 to 275°C, and approximately three CO_2 molecules are removed in the range from 275 to 375°C. The residue after calcination at 415°C corresponds to the composition CoO + $1/2Fe_2O_3$ (29.51%, calcd. 29.95%). The analysis of the gas phase shows three regions of CO_2 evolution: 240–310°C (29%), 340–370°C (29%), 340–370°C (2%), and 370–470°C (48.9%); CO (13.6%) is also evolved in the last region; and 29% CO_2 approximately correspond to one oxalate group.

Compound **III** loses water of crystallization below 160°C, ammonia elimination starts at 190°C, and about one CO_2 molecule is eliminated together with ammonia below 325°C. The continuous mass loss corresponding to $3CO_2 + 3CO$ occurs in the range from 325 to 540°C. The residue (30.18%) corresponds to the composition $CoCrO_3$ (calcd. 29.93%). A complicated double peak of CO_2 evolution (54.4%) and a complicated peak of CO evolution (32.8%) are observed in the ranges 250–470 and 330–540°C, respectively. The point experiments (Table 4) show that complexes **I** and **III** form $CoMC_4O_8 \cdot 2NH_3$ (M = Fe, Cr) in a range of 200–300°C similarly to the thermolysis of $[Co(NH_3)_6][Fe(CN)_6]$ [14]. Residual carbon corresponding to approximately one C_2O_4 group is observed at higher temperatures (below ~350°C) in the calcination residues. The products are amorphous to X-rays, i.e., highly dispersed. The amounts of ammonia and C_2O_4 found in the absorptive liquids are consistent with these data.

The thermolyses of compounds **II** and **IV** in argon are also very similar. Both complexes lose water of crystallization in the ranges 50–110°C (**II**) and 50–120°C (**IV**) and retain an unchanged composition on further heating to 220°C (**II**) and to 290°C (**IV**). According to the TG curve, compound **II** shows a smooth mass loss in the range from 220 to 600°C and compound **IV** undergoes the mass loss in the range from 290 to 800°C (Fig. 2). The mass loss in the range from 220 to 400°C for complexes **II** and **IV** corresponds to the loss of all coordinated En. Approximately one oxalate group (16–18%) is retained in the residue after calcination in the ranges 450–600 and 500–800°C for compounds **II** and **IV**, respectively. The residue after the calcination of complex **II** attains the composition $CoO + 1/2Fe_2O_3$ at 600°C, and the composition of the calcination residue for compound **IV** is $CoO+ 1/2Cr_2O_3$ at 800°C.

The point experiments (Table 4) show that complexes **II** (at 280°C) and **IV** (~380°C) retain about two En molecules, but a portion of coordinated oxalate is already decomposed. The analysis of the gas phase confirms that the destruction products of En and En itself are evolved indeed in the indicated temperature ranges. Only 22–28% of the En amount can be trapped, but a significant amount of organic products is lost via deposition in connecting hoses. In both cases, the amount of evolved CO is larger than that of CO_2 (Table 2). One complicated peak of CO evolution in the range from 370 to 600°C and two peaks of CO_2 evolution at 315–355°C and 375–530°C are observed for compound **II**. On the contrary, for complex **IV** CO is formed in the range from 370 to 470°C and from 470 to 590°C and continues up to 800°C, and CO_2 is formed with a maximum at 410°C ceasing at 525°C. Iron and intermetallic compound CoFe are detected by X-ray diffraction analysis for complex **II** at 480 and 600°C, respectively. Cobalt(II,III) oxide and chromium(II) oxalate are found for complex **IV** at 600 and 800°C, respectively. Thus, Co and Fe are reduced completely, probably, by oxalate, whereas cobalt is not reduced in the presence of chromium. Residual carbon is observed in the residues after the calcination of compounds **II** and **IV**, and its amount is ~20% of the initial carbon content in both cases.

Thus, the results of thermal analysis showed that four studied binary complexes in air behaved similarly and decomposed to form the sum of oxides of central ions. The binary complexes containing coordinated En completely decompose in air at the temperature by ~50°C higher than those containing coordinated ammonia, whereas for an argon atmosphere this temperature is higher by 200–300°C. The whole decomposition process in argon occurs in a broader (by 200–400°C) temperature range. The decomposition of complex **IV** ceases at the highest temperature. The experiments using the quantitative analysis of the gas flow (Table 2) to the contents of CO_2 and CO show that some portion of carbon is always evolved as CO in both air and argon. The temperature ranges of the isolation of carbon oxides in these media do not coincide. Almost all evolved coordinated ammonia and 80–90% of the calculated amount of CO_2 can be trapped upon thermolysis in air. For the thermolysis of the binary complexes with En as the destruction product of the latter, ammonia (about 30% of nitrogen contained in the complex) is formed. The test with Nessler's reagent shows that the absorptive solution contains ammonia but not En. The thermolysis of the (Co–Fe) complex gives metals + residual carbon as products, and the thermolysis products of the (Co–Cr) complex are the sum of metal oxides and residual carbon.

The point experiments on thermolysis in hydrogen (Table 5) established that complex **I** at 275°C lost all coordinated ammonia and a portion of oxalate and at 400 and 500°C complex **I** forms an almost pure mixture of intermetallic compound CoFe with Fe and Co. The same result was obtained for compound **II** at >600°C. It has earlier been shown [7] that at 525°C complex **III** forms a mixture of Co + $CoCr_2O_4$. At 275°C compounds **I** and **III** still remain two ammonia molecules. At 280°C the decomposition product of complex **II** has the same empirical formula $CoFe(En)_2(C_2O_4)_{2.25}O$, as for thermolysis in argon: the reflections corresponding to the initial complex appear in the diffraction pattern of the residue. Therefore, the residue should be considered as a mixture of the undecomposed initial complex with the products of its decomposition. In media of argon and hydrogen, complex **IV** does not give metallic cobalt upon reduction but forms a mixture of oxides. The thermolysis products of compound **III** in argon and in hydrogen at 350 and 275°C and compound **IV** at 380°C are partially dissolved in water and are dissolved without a residue in 25% hydrogen peroxide. This indicates that there are no oxide and metallic phases in these residues but they contain oxalates. The underestimated values of the amounts of evolved CO_2 in hydrogen can be explained by its partial reduction to hydrocarbons [7].

Thus, the thermolysis of binary complexes $[Co(NH_3)_6][Fe(C_2O_4)_3] \cdot 2H_2O$ in hydrogen gives a CoFe powder containing no carbon, and the thermolysis in air provides pure metal oxides. The products with a high content of residual carbon are formed in argon. The thermolysis in hydrogen does not allow binary complexes **II–IV** to get rid of residual carbon at temperatures rather low for the formation of highly dispersed products.

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