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Reaction of Cobalt(III) Diaquatetrammine Cation with 5-(3-Nitrophenyl)tetrazole

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Abstract—A series of cobalt(III) tetrazolate tetrammine complexes were prepared by reaction of cobalt(III) diaquatetraammine perchlorate with 5-(3-nitrophenyl)tetrazole. The factors affecting this reaction were studied. The reaction was thermally activated both by common heating with an external heater and microwave heating. Thermolysis of the tetrazolate complexes was studied.

At present, efforts made in coordination chemistry are aimed at development of known and searching for new procedures for preparing mono- and polynuclear complexes with heterocycles containing several nitrogen atoms [1, 2]. Among these compounds cobalt(III) tetrazolate ammine complexes exhibit valuable properties [3–5], in particular, fungicide and antibacterial power [6, 7]. Thus, development of procedures for preparing cobalt(III) tetrammine tetrazolates is an urgent problem.

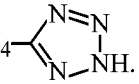
Suitable precursors for preparing cobalt tetrazolates are cobalt(III) diaquatetrammines (**I**). Water in these complexes is the most labile ligand and can be readily substituted by tetrazole derivatives [8].

We used 5-(3-nitrophenyl)tetrazole [5-(3-$NO_2C_6H_4$)-TetrH]. Since this compound exhibits acidic properties (pK_a 3.45), we suggested the possibility of its deprotonation during substitution of water molecules:

$$\underset{\mathbf{I}}{[Co(NH_3)_4(H_2O)_2]^{3+}(ClO_4^-)_3} + 2\,5\text{-}(3\text{-}NO_2C_6H_4)TetrH$$

$$\rightarrow \underset{\mathbf{II}}{\{Co(NH_3)_4[5\text{-}(3\text{-}NO_2C_6H_4)Tetr^-]_2\}^+ClO_4^-}$$

$$+ 2HClO_4 + 2H_2O.$$

5-(3-$NO_2C_6H_4$)TetrH = 3-$NO_2C_6H_4$–


The reaction is usually performed on heating at 90–100°C for 2–3 h [9]. Initially the reaction between **I** and 5-(3-nitrophenyl)tetrazole was performed in 5% perchloric acid by heating on a boiling water bath for 3 h. In 2 h the initial diaqua complex is completely consumed to form almost equal amounts of the target product *cis*-tetramminebis[5-(3-nitrophenyl)tetrazolato]cobalt(III) perchlorate **II** and $\{Co_2(NH_3)_8[5\text{-}(3\text{-}NO_2C_6H_4)Tetr](H_2O)_2\}(ClO_4)_5 \cdot 2H_2O$ (**III**). In complex **III** the 5-(3-nitrophenyl)tetrazolate ligand is a bridge between two Co^{3+} cations. We found that only complex **III** is formed in the first steps of the reaction, and complex **II** is formed only after a definite amount of **III** is accumulated.

Thus, the reaction between **I** and 5-(3-nitrophenyl)-tetrazole is a multistage process. In the first step the dimer where the tetrazolate ligand is a bridge between two Co^{3+} cations is formed. Then the Co–N bond is ruptured and the second aqua ligand is substituted with 5-(3-nitrophenyl)tetrazolate anion. The fact that 5-R-tetrazoles can be coordinated by two nitrogen atoms confirms this assumption [10–13]. However, formation of complexes with bridging water ligands is also possible. Exact determination of the structure of complex **III** requires additional study.

Recently microwave heating has found increasing use for thermal activation of chemical reactions [14]. A chemical system containing polar molecules and ions can absorb UHF radiation and transform it into heat. Tselinskii *et al.* [15, 16] found that substitution reactions are accelerated on exposure to microwave radiation owing to “nonthermal” effects. In some cases UHF heating not only accelerates a chemical reaction but also gives results that differ qualitatively and quantitatively from those obtained with the conventional thermal activation.

Anation reaction of Co(III) ammine complexes is accelerated on microwave heating [17]. However, the nature of “nonthermal” effects is not understood. On microwave heating for 1 h the reaction between **I** and 5-(3-nitrophenyl)tetrazole also yields **II** and **III**.

Thermal analysis of complexes **II** and **III**[*]

Thermolysis products	Temperature range, °C	Residue, %		Peak temperature, °C	Width of temperature peak, °C
		found	calculated		
$[Co(C_7H_4O_2N_5)_2(NH_3)_4]ClO_4$					
	30–230			145	60–185
$Co(C_7H_4O_2N_5)_2ClO_4$		87.9	88.5		
	230–306			285	245–306
$Co(C_7H_4O_2N_5)O$		44.3	43.7		
	306–430			347	320–405
				410	408–430
$1/2Co_2O_3$	>430	15.8	13.7		
$[Co_2(C_7H_4O_2N_5)(NH_3)_8(H_2O)_2](ClO_4)_5 \cdot 2H_2O$					
	40–142			75	60–135
$Co_2(C_7H_4O_2N_5)(NH_3)_8(ClO_4)_5$		92.0	92.9		
	142–244				
$Co_2(C_7H_4O_2N_5)(ClO_4)_5$		80.0	79.5		
	244–326			275	245–315
Co_2O_3	>326	13.1	16.3		

[*] Data on transition temperatures are placed between the rows corresponding to the initial substance and product of a given transition.

However, the content of **II** in the reaction mixture substantially increased. The yield of **II** was higher by 18% as compared to the conventional heating. This can be only in part due to different temperature conditions. On microwave heating the reaction mixture vigorously boils at ~102°C. In the case of conventional heating a boiling water bath was used. Thus, microwave heating increases the yield of **II** and considerably decreases the reaction time.

A study of thermolysis of cobalt tetrazolate complexes is an urgent problem since only a small number of these compounds were examined in this respect.

Thermolysis of complexes **II** and **III** was studied under dynamic conditions at a heating rate of 5 deg min^{-1}. Intense thermal decomposition of **III** was found to start at temperatures higher than 230°C (see table).

In the TGA curve of **II** a blurred endothermic peak in the range 60–185°C is characterized by a 12% weight loss and is probably due to elimination of four ammonia lignads.

Then the sample melts at 230°C. The second exothermic peak is observed at 245–306°C and can be divided into peaks corresponding to 21 and 35% weight loss of the sample. We assign these peaks to melting of the nitrophenyltetrazole ligands and their decomposition by oxidation with intraspheric perchlorate anions with rearrangement of the inner coordination sphere of the complex.

The next two exothermic effects at 320–405 and 408–430°C are accompanied by a 17% weight loss and are assigned to oxidation of the remaining ligands with perchlorate anions and their decomposition. This peak is gradually transformed into the last exothermic peak accompanied by a 11% weight loss. This is probably due to formation of Co_2O_3 (which is usually formed in decomposition of cobalt(III) complexes in air [18]) and its decomposition.

Complex **III** containing 5-(3-nitrophenyl)tetrazolate bridging ligand is more thermally stable. Its intense decomposition starts at 244°C.

As determined by thermal analysis, crystallization and coordinated water are eliminated from this complex simultaneously in the range 60–142°C, which is accompanied by a 8% weight loss. It should be noted that thermal analysis of cobalt(III) ethylenediamine diaqua complexes showed that in the *cis* isomers of these compounds all four water molecules are eliminated simultaneously and in the *trans* isomers the crystallization and coordinated water is eliminated separately [19]. This confirms the *cis* structure of complexes **II** and **III**.

In the next step ammonia molecules are eliminated at 160–230°C, which results in a 14% weight loss of the sample. Strong exothermic peak in the range 244–326°C in the DTA curve of complex **III** is due to intraspheric degradation of the complex and oxidation of 5-(3-nitrophenyl)tetrazolate ligands with intraspheric perchlorate anions. In this case the weight loss is as high as 66%. We suggest formation and decomposition of Co_2O_3 in this step.

The results of thermal analysis of **II** and **III** are presented in the table.

The kinetic parameters of thermolysis of these complexes were determined by differential scanning calorimetry. The onset temperature of intense decomposition (°C), the peak temperature (°C), the logarithm of the pre-exponential factor in the Arrhenius equation, and the thermolysis activation energy (kJ mol^{-1}) at the onset temperature of intense thermolysis of complex **II** are 230, 287.1, 34.6 ± 0.7, and 183.1 ± 3.6, respectively. For complex **III** these parameters are 244, 276.4, 59.0 ± 1.3, and 290.0 ± 6.3, respectively. The thermolysis kinetics of the cobalt complexes confirms indirectly their structure: Thermolysis of **III** starts at higher temperatures but occurs more intensely. This is probably due to strong distortion of the octahedral surrounding of Co(III) in complex **III** containing tetrazolate bridges.

Thus, thermolysis of complexes **II** and **III** under nonisothermal conditions is a multistage process. In the first step deaquation and elimination of ammonia ligands results in degradation of the inner coordination sphere of the complex. Then tetrazolate ligands decompose, with their oxidation with the perchlorate anions in the final steps.

EXPERIMENTAL

The IR spectra of thin layers of the samples were recorded on a Specord M-80 spectrophotometer. The ^1H NMR spectra were recorded on a Perkin–Elmer R-12 spectrometer operating at 60 MHz, with HMDS as the internal reference. The reaction course was monitored by TLC on Silufol UV-254 plates. The eluent was 3% aqueous solution of sodium perchlorate.

The UHF heater consists of a short-circuited wave guide with 9 × 4.5-cm section, connected with a UHF generator (600 W output power and 2450 MHz working frequency). The reactor (glass test tube 35 mm in diameter, equipped with a thermometer and a reflux condenser) was placed in a special hole in the wave guide.

The thermal analysis was performed on a Paulik–Paulik–Erdey device. The heating rate was 5 deg min^{-1}. The calorimetric experiments were performed under argon on a Perkin–Elmer DSC-7 differential scanning calorimeter. The heating rate was 10 deg min^{-1}.

Cobalt(III) diaquatetrammine perchlorate (**I**) prepared by the procedure in [20] and was used for synthesis of **II** and **III** without isolation from the solution.

***cis*-Tetramminebis[5-(3-nitrophenyl)tetrazolato]-cobalt(III) perchlorate II.** 5-(3-Nitrophenyl)tetrazole (1 g) was added to a solution of complex **I** (0.5 g) in 5% perchloric acid. The suspension was heated on a boiling water bath for 3 h and cooled to room temperature. After 2 days the precipitate was filtered off and washed with ethanol (2 × 5 ml). The yield of **II** was 0.5 g (53%). IR spectrum, ν, cm^{-1}: 1576 m, 1280 m (NH_3, Tetr), 1076 m (ClO_4), 1552 s (NO_2), 832 m (Ar). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 8.0, 7.35 m (8H, ArH), 4.45, 3.55 (12H, NH_3). Found, %: C 28.2; H 3.8; N 32.3. $C_{14}H_{20}ClCoN_{14}O_8$. Calculated, %: C 27.7; H 3.3; N 32.3.

The volume of the mother liquor was reduced by half by evaporation. The crystalline precipitate that formed after cooling was filtered off. The yield of complex **III** (dihydrate) was 0.3 g (34%). IR spectrum, ν, cm^{-1}: 3312, 3152 m (H_2O), 1620, 1348 m (NH_3, Tetr), 1092 s (ClO_4), 1552 m (NO_2), 838 w (Ar). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 8.14, 7.4 m (4H, ArH), 5.5 (24H, NH_3). Found, %: C 7.8; H 3.9; N 18.5. $C_7H_{36}Cl_4Co_2N_{13}O_{26}$. Calculated, %: C 8.3; H 3.6; N 18.0.

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