

Structure and Thermal Characteristics of Bis(triethylammonium)-tetrakis(3,5-dinitro-2-pyridonato)cobalt(II)

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Abstract—The ionic compound $[\text{Co}(\text{OC}_5\text{H}_2\text{N}(\text{NO}_2)_2)_4]((\text{C}_2\text{H}_5)_3\text{NH})_2$ (**I**) was synthesized by the reaction of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ with 2-hydroxy-3,5-dinitropyridine in acetonitrile in the presence of triethylamine as a deprotonating agent. The structure of compound **I** was studied by X-ray diffraction (CCDC no. 2196071) and thermodynamic characteristics of **I** were determined.

Keywords: cobalt(II), 2-hydroxy-3,5-dinitropyridine, structure, thermal properties

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INTRODUCTION

Pyridonate, pyridonate-carboxylate, and other mixed-anion (heteroanion) complexes of 3d metals attract increasing attention of specialists in coordination chemistry. The pyridonate anion has a triatomic N—C—O bridge, which forms stable metal cages of polynuclear complexes much more often than does the conformationally flexible O—C—O group of the carboxylate anion. Variation of the properties of aliphatic or aromatic monocarboxylate anions is often accomplished by introducing various substituents into the aliphatic chain or aromatic ring. The properties of 2-hydroxypyridine can be changed in a similar way. The possibilities of introduction of electron-withdrawing substituents into this molecule are quite limited. For example, it is impossible to attain the same effects that arise on going from the phenyl to pentafluorophenyl group. However, by using strong electron-withdrawing substituents, it is possible to attain significant effects even for 2-hydroxypyridine. Thus the acidity of 2-hydroxy-3,5-dinitropyridine is seven orders of magnitude higher than that of unsubstituted 2-hydroxypyridine (pK_a of 4.41 vs. 11.62).

The interest in cobalt coordination compounds with organic ligands is caused by the fact that they can be used in various high-temperature techniques to obtain cobalt oxides. The most stable spinel type cobalt oxide Co_3O_4 is a *p*-type semiconductor [1, 2], which is used as an electrode material in supercapacitors [2, 3], anode for Li ion batteries [4], and a popular

heterogeneous catalyst [5–7]. The presence of cobalt in two oxidation states +2 and +3 and low binding energy of oxygen chemisorbed on the Co_3O_4 surface account for the high activity of this oxide in reactions with the gas phase and determine its applicability as the working medium in chemical sensors for xylene, ethanol, methanol, acetone, CO, H_2 , CH_4 , NH_3 , H_2S , and NO_x [8–16]; however, the sensing properties of Co_3O_4 -based materials have been little studied. Cobalt oxide CoO is used as a pigment for glass and ceramics and in electrochemistry and possesses magnetic, catalytic, and sensing properties [17–19].

This study addresses the synthesis, structure, thermal stability, composition of the gas phase, and determination of thermodynamic characteristics of the cobalt(II) compound $[\text{Co}(\text{OC}_5\text{H}_2\text{N}(\text{NO}_2)_2)_4]((\text{C}_2\text{H}_5)_3\text{NH})_2$.

EXPERIMENTAL

The new cobalt(II) coordination compound was synthesized in air using acetonitrile CH_3CN (special purity grade, Khimmed) without additional purification. The commercial chemicals, cobalt(II) chloride hexahydrate $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Laverna, analytical grade) and triethylamine $(\text{C}_2\text{H}_5)_3\text{N}$ (Acros Organics, 99%), were used for the synthesis. 2-Hydroxy-3,5-dinitropyridine $\text{HOC}_5\text{H}_2\text{N}(\text{NO}_2)_2$ was prepared by a known procedure [20].

Table 1. Selected bond lengths (*d*) and bond angles (ω) of compound **I**

Bond	<i>d</i> , Å
Angle	ω , deg
Co(1)–O(6)	2.288(5)
Co(1)–O(1)	2.409(5)
Co(1)–N(10)	2.094(6)
Co(1)–N(1)	2.102(6)
Co(1)–N(4)	2.113(6)
Co(1)–N(7)	2.121(6)
O(6)Co(1)O(1)	130.73(19)
N(10)Co(1)O(6)	135.3(2)
N(10)Co(1)O(1)	81.7(2)
N(10)Co(1)N(1)	90.6(2)
N(10)Co(1)N(7)	87.8(2)
N(10)Co(1)N(4)	164.5(2)
N(1)Co(1)O(6)	85.7(2)
N(1)Co(1)O(1)	58.30(19)
N(1)Co(1)N(7)	178.3(2)
N(1)Co(1)N(4)	93.2(2)
N(7)Co(1)O(6)	95.1(2)
N(7)Co(1)O(1)	121.9(2)
N(4)Co(1)O(6)	60.0(2)
N(4)Co(1)O(1)	87.6(2)
N(4)Co(1)N(7)	88.5(2)

Elemental analysis was performed on a Carlo Erba EA 1108 automatic C,H,N-analyzer. IR spectra were measured on a Perkin-Elmer Spectrum 65 Fourier Transform IR spectrophotometer by the attenuated total reflectance (ATR) technique in the frequency range of 400–4000 cm^{−1}.

Synthesis of [Co(OC₅H₂N(NO₂)₂)₄]((C₂H₅)₃NH)₂ (I). Weighed amounts of CoCl₂·6H₂O (0.050 g, 0.21 mmol) and HOC₅H₂N(NO₂)₂ (0.078 g, 0.42 mmol) were dissolved in CH₃CN (5 mL) at room temperature. Then (C₂H₅)₃N (0.08 mL, 0.58 mmol) was added to the reaction solution. The resulting solution was left for slow evaporation at room temperature.

The square-prismatic orange crystals suitable for X-ray diffraction that appeared within 3 days were separated from the mother liquor by decantation, washed with cold CH₃CN, and dried in air. The yield of **I** was 0.052 g (49% based on HOC₅H₂N(NO₂)₂).

For C₃₂H₄₀N₁₄O₂₀Co (**I**)

Anal. calcd., % C, 37.07 H, 4.03 N, 19.62
Found, % C, 38.45 H, 4.12 N, 19.06

IR (ATR; ν , cm^{−1}): 3084 m, 3001 w, 2887 w, 2815 br.w, 2492 br.w, 1607 vs, 1574 w, 1547 m, 1512 w, 1479 m, 1427 s, 1374 m, 1312 vs, 1257 vs, 1191 m, 1161 w, 1112 s, 1058 w, 1013 m, 942 m, 828 m, 750 m, 709 s, 632 m, 526 br.m, 449 w, 424 br.m.

The X-ray diffraction study of complex **I** was carried out at 150 K on a Bruker ApexII DUO diffractometer (CCD detector, MoK_α, λ = 0.71073 Å, graphite monochromator). The structure was solved using the ShelXT software [21] and refined using full-matrix least-squares method with the Olex2 program [22] in the anisotropic approximation for non-hydrogen atoms. The NH hydrogen atoms were located from difference Fourier maps, the positions of the other hydrogen atoms were calculated geometrically, and all H atoms were refined in the isotropic approximation using the riding model. The crystallographic parameters and structure refinement details for compound **I** were the following: C₃₂CoH₄₀N₁₄O₂₀, *M* = 999.71 g/mol, orange crystals, space group *P*2₁/*n*, *a* = 13.8293(10), *b* = 13.4844(11), *c* = 22.8520(16) Å, β = 90.494(3)°, *V* = 4261.3(6) Å³, *Z* = 4, ρ (calcd.) = 1.558 g cm^{−3}, μ = 5.00 cm^{−1}, 29203 measured reflections, 7668 reflections with *I* > 2σ(*I*), *R*_{int} = 0.0744, GOOF = 1.112, *R*₁ (*I* > 2σ(*I*)) = 0.1190, *wR*₂ (*I* > 2σ(*I*)) = 0.3239, *T*_{min/max} = 0.929/0.952. Selected bond lengths (*d*) and bond angles (ω) of compound **I** are presented in Table 1 and the geometric parameters of hydrogen bonds are given in Table 2.

The atom coordinates and other parameters of structure **I** were deposited with the Cambridge Crystallographic Data Centre (CCDC no. 2196071; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Table 2. Geometric parameters of hydrogen bonds in compound **I**

D–H···A contact	Distance, Å			DHA angle, deg
	D–H	H···A	D···A	
N(14)–H(14)…O(16)	1.00	1.93	2.848(7)	151.00
N(14)–H(14)…O(17)	1.00	2.55	3.326(9)	134.00
N(13)–H(13A)…O(11)	1.00	1.86	2.797(8)	154.00
N(13)–H(13A)…O(12)	1.00	2.31	2.977(9)	123.00

Table 3. Mass spectrum of the gas phase of complex **I** at different temperatures

<i>m/z</i>	Ion	Intensity, %	
		<i>T</i> = 412 K	<i>T</i> = 384 K
86	$[(C_2H_5)_3N-15]^+$	100	100
57	$[C_2H_5NCH_2]^+$	61	38
122	$[(C_5H_2NNO_2)]^+$	5	
138	$[(C_5H_2ON)NO_2]^+$	4.4	2
154	$[(C_5H_2OON)NO_2]^+$	1.6	
168	$[(C_5H_2N)(NO_2)_2]^+$	20	18
184	$[(C_5H_2NO)(NO_2)_2]^+$	45	50

The geometry of cobalt polyhedron was analyzed using the SHAPE 2.1 software [23].

The thermal behavior of **I** was studied by simultaneous thermal analysis (STA) involving recording of both thermogravimetry (TG) and differential scanning calorimetry (DSC) curves in an argon atmosphere. The measurements were carried out on an STA 449 F1 Jupiter instrument (NETZSCH) in aluminum crucibles covered with lids provided with holes to maintain the vapor pressure of 1 atm during the thermal decomposition of samples. The sample was heated up to 500°C at a rate of 10°C/min. The sample weight was 7.09 mg. The accuracy of temperature measurement was $\pm 0.7^\circ\text{C}$ and the accuracy of weight determination was $\pm 1 \times 10^{-2}$ mg. The TG and DSC curves were measured using the correction file and temperature and sensitivity calibrations for the specified temperature program and heating rate. After thermal analysis, scanning electron microscopy images were obtained on a Zeiss NVision 40 high-resolution scanning electron microscope with an accelerating voltage of 1 kV using an InLense detector. Energy dispersive X-ray (EDX) spectra were recorded using an Oxford Instruments X-MAX 80 mm² attachment with an accelerating voltage of 20 kV. The magnification was up to $\times 30000$.

The vaporization of the complex was studied in the temperature range of 300–700 K on an MC 1301 mass spectrometer. The standard molybdenum Knudsen effusion cells with an evaporation-to-effusion area ratio ≥ 600 were used. The temperature was measured by a Pt–Pt/Rh thermocouple and maintained constant to an accuracy of $\pm 1^\circ\text{C}$. The main ion intensities recorded in the mass spectrum of saturated vapor at various temperatures of the effusion cell are given in Table 3.

RESULTS AND DISCUSSION

The reaction of cobalt(II) chloride hexahydrate with 2-hydroxy-3,5-dinitropyridine in the presence of

$(C_2H_5)_3N$ as deprotonating agent in acetonitrile gave an ionic compound with a complex anion, $[\text{Co}(\text{OC}_5\text{H}_2\text{N}(\text{NO}_2)_2)_4]((C_2\text{H}_5)_3\text{NH})_2$ (**I**). According to X-ray diffraction data, the isolated compound **I** crystallizes in the monoclinic space group $P2_1/n$. The cobalt(II) ion in the dianion occurs in the coordination environment of four nitrogens (Co(1)–N, 2.094(6)–2.121(6) Å) and two oxygens (Co(1)–O(10), 2.845(14) and 2.845(14) Å) of the four 3,5-dinitro-2-pyridonate anions (Fig. 1, Table 1), which form the CoN_4O_2 polyhedron shaped like a distorted trigonal prism ($S_q(D_{3h}) = 6.489$, $S_q(O_h) = 8.604$). Two 3,5-dinitro-2-pyridonate anions act as chelating ligands, thus forming the –Co–N–C–O– four-membered ring, while the other two anions are coordinated in the monodentate fashion via only the pyridine nitrogen atom. In ionic compound **I**, the proton of each triethylammonium cation $(C_2\text{H}_5)_3\text{NH}^+$ is hydrogen-bonded to the oxygen atoms of the hydroxyl group and one nitro group of the modonenate 3,5-dinitro-2-pyridonate anion in $[\text{Co}(\text{OC}_5\text{H}_2\text{N}(\text{NO}_2)_2)_4]^{2-}$ (N...O, 2.797(8)–3.326(9) Å; OHO, 123.00°–154.00°, Table 2). In the crystal packing of **I**, the $[\text{Co}(\text{OC}_5\text{H}_2\text{N}(\text{NO}_2)_2)_4]^{2-}$ dianions and the $(C_2\text{H}_5)_3\text{NH}^+$ cation alternate along the *c* axis, while each conditional ion layer stretched along the *b* axis is oppositely directed (Fig. 2).

The thermal behavior of **I** was studied by STA under argon with simultaneous recording of TG and DSC curves up to 500°C (Fig. 3). The thermolysis consists of three main stages. The first stage is accompanied by insignificant endothermic peak at 194°C (Fig. 3b, peak a) and no weight change, which may be attributable to the start of sample melting. At higher temperature, the next stage takes place, which is accompanied by a strong exotherm with a peak at 221.5°C (Fig. 3b, peak b) and a pronounced weight loss of 54.31% relative to the initial sample weight. The third stage is characterized by a minor exotherm over an extended temperature range (289.5–357.2°C; Fig. 3b, peak c) accompanied by the next weight loss

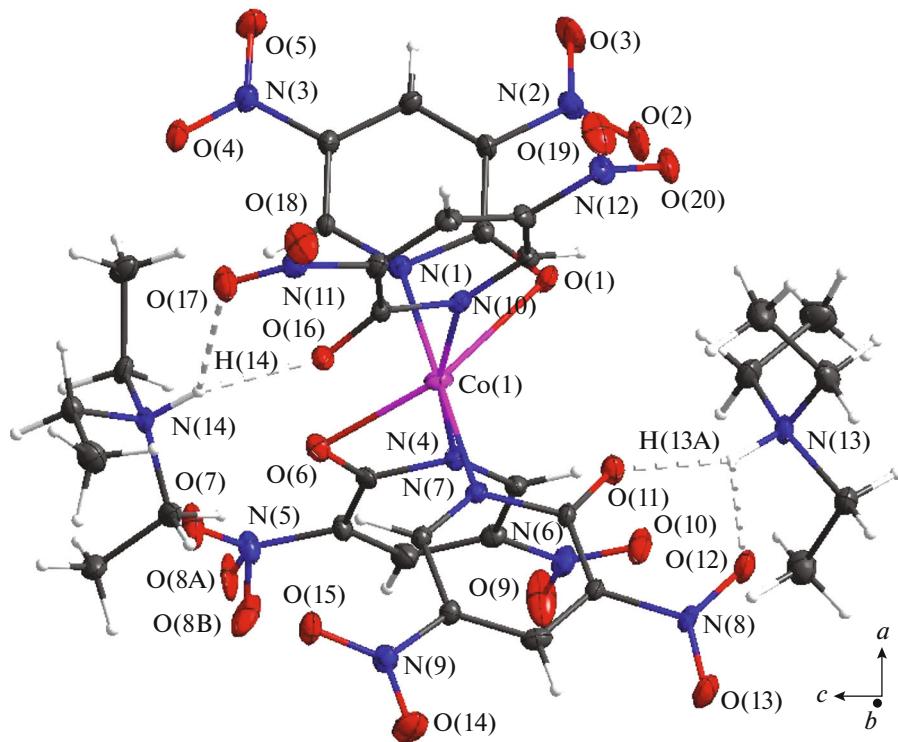


Fig. 1. Molecular structure of **I**. Non-hydrogen atoms are shown as thermal ellipsoids ($p = 30\%$), and dashed lines depict hydrogen bonds.

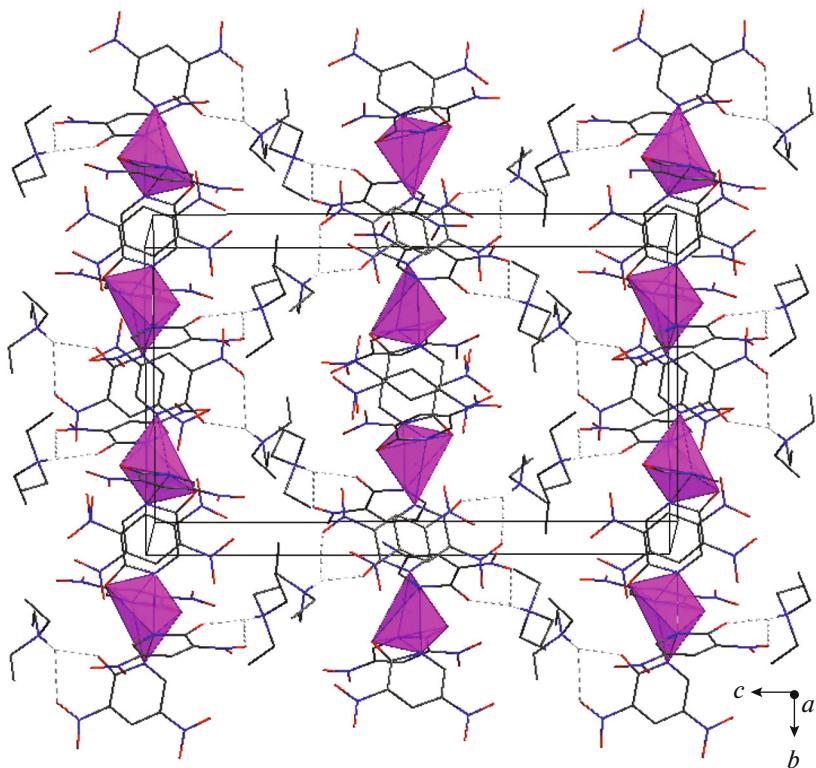


Fig. 2. Fragment of the crystal packing of **I**. The C–H hydrogen atoms are omitted for clarity; the hydrogen bonds are depicted by dashed lines.

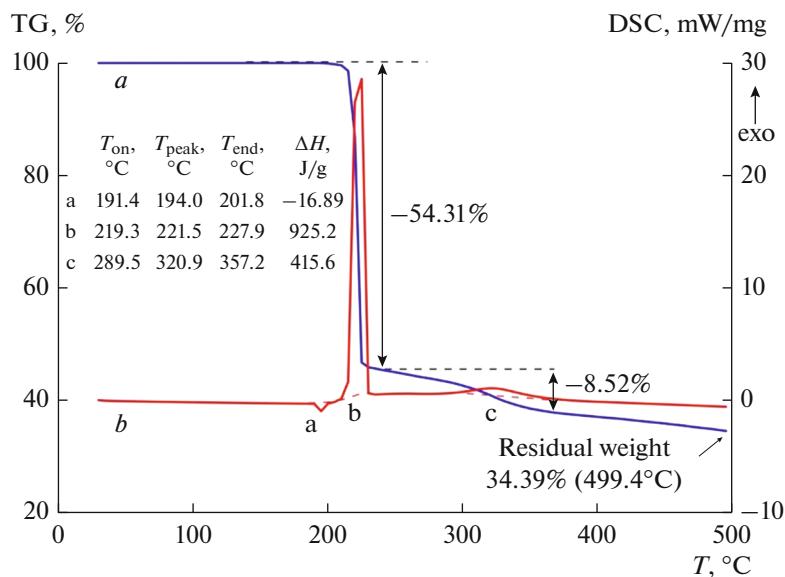


Fig. 3. (a) TG and (b) DSC curves of **I**.

($m_{exp} = 8.52\%$). Subsequently, a minor weight change takes place, and the weight remaining by 500°C is equal to 34.39% of the original sample weight.

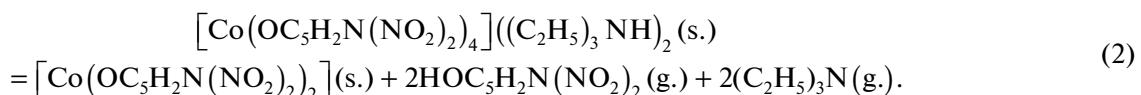
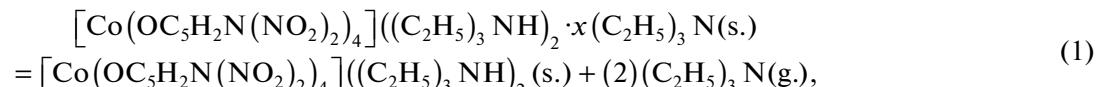
The composition of the final compound **I** was determined by EDX analysis and by analysis of the micromorphology (Fig. 4) of the residual substance. The weight of the residue after thermolysis points to a highly carbonized product containing cobalt oxide. The experimental results show the following composition of the thermolysis product: C (75.73%), O (21.67%), and Co (2.59%).

Subsequently, we investigated the vaporization of the complex by the Knudsen effusion method with mass-spectral analysis of the gas phase in the temperature range of 300–700 K. Analysis of the experimental data summarized in Table 3 provides the conclusion that vaporization of the cobalt(II) complex includes transition of the 3,5-dinitro-2(H)-pyridone and triethylamine molecules to the gas phase. In order to clarify the character of vaporization and calculate the partial pressures, we conducted an experiment on complete evaporation of a known weighed amount of the complex at two different temperatures. The results of this experiment are presented in Fig. 5.

The initial ion current intensity $I_{[(C_2H_5)_3N-15]}^+$ at $T = 382$ K monotonically decreases, corresponding to transition of triethylamine molecules to the gas phase. The subsequent ion current intensities $I_{[(C_5H_2NO)(NO_2)_2]}^+$, $I_{[(C_2H_5)_3N-15]}^+$, at $T = 406$ K remain virtually constant, being due to the transition of triethylamine ($C_2H_5)_3N$ and 2-hydroxy-3,5-dinitropyridine $HOC_5H_2(NO_2)_2$ molecules to the gas phase. After a definite period of time, the ion current intensities start to monotonically

decrease in parallel until they vanished. This picture reflects the partial burning out of the sample of **I**. After completion of this part of the experiment, the non-volatile residue remains in the effusion cell in an amount of 35% of the initial sample weight; this suggests that the non-volatile residue is cobalt(II) 3,5-dinitro-2-pyridonate $[Co(OC_5H_2N(NO_2)_2)_2]$. These results are in good agreement with thermogravimetric data, according to which the weight of the non-volatile residue in the first two stages of thermal decomposition of the complex is 34.39% of the initial sample weight.

For determining the source of $(C_2H_5)_3N$ in the gas phase in the first stage of thermal decomposition in vacuum, the crystals were annealed at 160°C. This temperature is markedly higher than the temperature at which $(C_2H_5)_3N$ is vaporized when the compound is evaporated in vacuum. This temperature was chosen on the basis of DSC data and was below 191.4°C, which is the temperature of the beginning of the first minor endotherm. When the crystals of the starting complex were kept at this temperature for 30 min in a water-jet pump vacuum, the color of the compound slightly changed. Analysis of the IR spectra and X-ray diffraction study of the annealed crystals showed that this was the starting compound **I**. Hence, the above-mentioned appearance of $(C_2H_5)_3N$ in the gas phase upon evaporation in vacuum is, most likely, due to its desorption from the crystal surface. No transformations of the initial complex take place at this temperature. Thus, the process can be described by the following two heterogeneous reactions:



Here, it should be noted that the gaseous products resulting from vaporization of cobalt(II) complex (reaction (2)), that is, the acid and the amine, correspond to the products of sublimation of the ammonium or amine salts, which are always sublimed congruently; hence, the saturated vapor partial pressures of triethylamine and 3,5-dinitro-2(H)-pyridone molecules should be equal in a confined space, or the molecular fluxes of these compounds upon vaporization from the effusion cell should be equal.

Data on the isothermal sublimation of the cobalt complex and congruent vaporization of triethylam-

monium 3,5-dinitro-2-pyridonate $\text{C}_5\text{H}_2\text{NO}(\text{NO}_2)_2\text{-(C}_2\text{H}_5)_3\text{NH}$ combined with the Hertz-Knudsen equation and with the basic equation of mass spectrometry

$$q_i = k/\sigma_i S_{\text{eff}} (TM_j/2\pi R)^{1/2} \int_0^t I_j dt, \quad (3)$$

$$p_j = k_j I_j T, \quad (4)$$

where S_{eff} is the effective area of effusion, k_j is the instrument constant, M_j is the molar mass of the j th component of the gas phase, t is the sublimation time, σ_j is the total ionization cross-section of the j th component of the gas phase, I_j is the total ion current resulting from ionization of the j th component of the gas phase, and T is the sublimation temperature, were used to calculate the absolute saturated vapor partial pressures above the cobalt complex. The results of the calculations are summarized in Table 4, which also gives the partial pressures (asterisked) corresponding to the minimum total pressure, i.e., for sample sublimation in a confined space.

The temperature dependences of the ion current intensities $I_{[(\text{C}_2\text{H}_5)_3\text{N}-15]}^+$, $I_{[(\text{C}_5\text{H}_2\text{NO})(\text{NO}_2)_2]}^+$ in the 350–

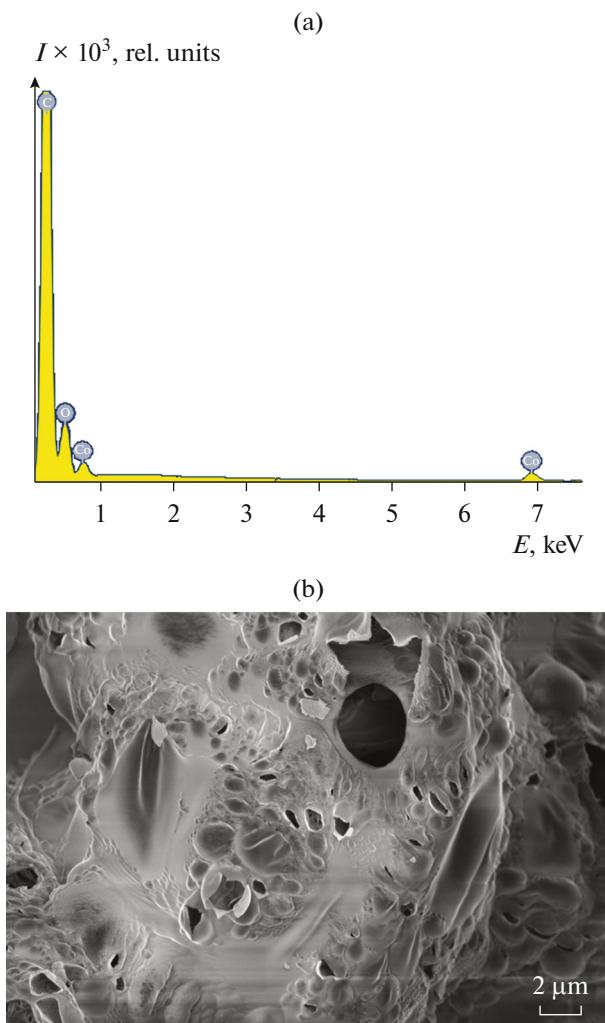


Fig. 4. (a) Energy dispersive X-ray spectrum and (b) micromorphology image ($\times 10000$ times) of the residue of I.

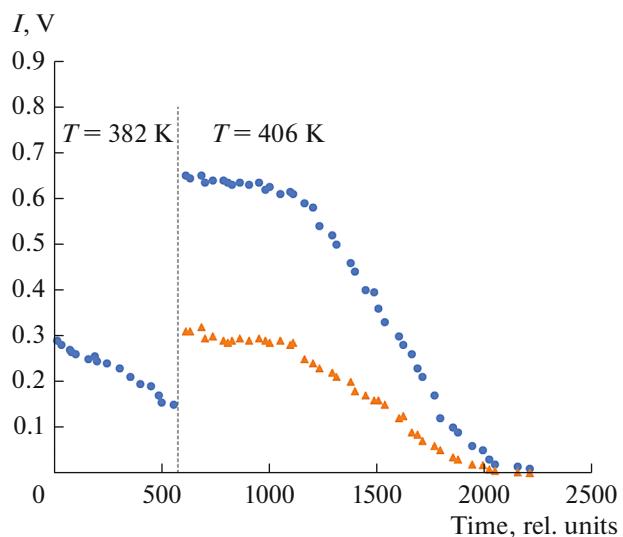


Fig. 5. Complete sublimation isotherm for the sample of the cobalt complex: (●) $I_{[(\text{C}_2\text{H}_5)_3\text{N}-15]}^+$, (▲) $I_{[(\text{C}_5\text{H}_2\text{NO})(\text{NO}_2)_2]}^+$.

Table 4. Partial pressures (Pa) of triethylamine (p_2) and 3,5-dinitro-2(H)-pyridone (p_1)

Sublimation conditions	Pressure			Temperature, K
	p_1	p_2	total	
Knudsen	3.75×10^{-3}	2.86×10^{-3}	6.61×10^{-3}	382
Confined space	$*3.27 \times 10^{-3}$	$*3.27 \times 10^{-3}$	$*6.54 \times 10^{-3}$	
Knudsen	1.18×10^{-1}	0.90×10^{-1}	2.08×10^{-1}	406
Confined space	$*1.03 \times 10^{-1}$	$*1.03 \times 10^{-1}$	$*2.06 \times 10^{-1}$	

* Corresponds to the minimum total pressure.

Table 5. Enthalpies of sublimation of $(C_2H_5)_3N$ and $HO(C_5H_2N)(NO_2)_2$ molecules from the condensed phase of the cobalt complex*

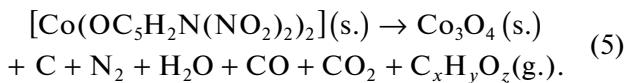
$\Delta_S H^0(T)$, kJ/mol		
$[(C_2H_5)_3N-15]^+$	$[(OC_5H_2N)(NO_2)_2]^+$	Temperature range, K
148.9 ± 6.8	141.9 ± 1.4	353–425
133.5 ± 14.8	129.7 ± 0.8	350–430
149.9 ± 5.7	149.9 ± 1.7	353–427
149.6 ± 5.4	133.8 ± 11.7	352–422
132.4 ± 5.9	131.6 ± 2.3	355–420
Average 142.9 ± 11.9	Average 137.9 ± 9.1	

* Recommended value: 140.4 ± 14.0 kJ/mol.

430 K range were used to calculate the enthalpy of sublimation of triethylamine and 3,5-dinitro-2-pyridone from the condensed phase of the cobalt complex by the Clausius–Clapeyron equation and the least squares method (Table 5). The enthalpy values obtained for various ions agree with each other within the determination errors. This result, in combination with data of Table 4, can be considered as direct evidence for the congruent nature of vaporization of triethylammonium 3,5-dinitro-2-pyridonate. The recommended enthalpy value given in Table 5 was obtained as the arithmetic mean over all independent experiments. According to this value, the enthalpy of heterogeneous reaction (2) is $\Delta H_T^\circ = 561.6 \pm 23.7$ kJ/mol.

We were unable to quantitatively describe the vaporization of bis(3,5-dinitro-2-pyridonato)cobalt(II) $[Co(OC_5H_2N)(NO_2)_2]_2$. When the sublimation of triethylammonium 3,5-dinitro-2-pyridonate (reaction (2)) was over, a poorly volatile bis(3,5-dinitro-2-pyridonato)cobalt(II) was left in the effusion cell. Noticeable vaporization (thermal decomposition) of the latter compound started at a temperature of >530 K. This was indicated by high ionic intensities of the peaks with $m/z = 14, 18, 28, 44$, which correspond to the H_2O , N_2 , CO , CO_2 molecules, etc., in the mass spectrum. After a certain period of time at 650 K, the intensity of ionic currents decreased down to the

background values of the instrument. The subsequent gradual increase in the temperature of the effusion cell to 700 K did not induce any noticeable changes in the mass spectrum of the residual gas phase in the mass spectrometer. The observed picture attests to the end of the thermal decomposition of $[Co(OC_5H_2N)(NO_2)_2]_2$. After completion of this part of the experiment, a non-volatile residue remained in the effusion cell. According to powder X-ray diffraction data, this was a gray-black amorphous phase and, according to X-ray fluorescence analysis, it contained cobalt. Since the weight of the amorphous phase amounted to 35% of the total weight of the initial complex, presumably, the final products were carbon and mixed cobalt oxide Co_3O_4 , and the third stage of thermal decomposition can be represented as reaction (5), which is in good agreement with the results of EDX analysis.



The experiment on the complete isothermal sublimation of the cobalt complex confirmed that bis(triethylammonium) tetrakis(3,5-dinitro-2-pyridonate)cobalt(II) contained a small amount of excess triethylamine. This fact can be attributed either to the formation of a stable non-stoichiometric compound such as a solid solution based on bis(triethylammo-

nium)-tetrakis(3,5-dinitro-2-pyridonato)cobalt(II) and triethylamine $[\text{Co}(\text{OC}_5\text{H}_2\text{N}(\text{NO}_2)_2)_4] \cdot ((\text{C}_2\text{H}_5)_3\text{NH})_2 \cdot x(\text{C}_2\text{H}_5)_3\text{N}$ (in this case, $x = 0.2$) or to the adsorption of triethylamine on the crystal surface. Thus, we determined thermodynamic characteristics of bis(triethylammonium)-tetrakis(3,5-dinitro-2-pyridonato)cobalt(II), demonstrated its vaporization as triethylammonium 3,5-dinitro-2-pyridonate molecule and the bis(3,5-dinitro-2-pyridonato)cobalt(II) condensed phase (reaction (2)), and described its composition as the adduct $[\text{Co}(\text{O}(\text{C}_5\text{H}_2)(\text{NO}_2)_2)_2] \cdot 2[(\text{C}_2\text{H}_5)_3\text{NHOC}_5\text{H}_2(\text{NO}_2)_2]$.

In conclusion, note that this cobalt complex can be considered as a promising material for the design of gas sensors in which the working medium is the amorphous cobalt oxide Co_3O_4 .

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

- Gu, F., Li, C., Hu, Y., and Zhang, L., *J. Cryst. Growth*, 2007, vol. 304, no. 2, p. 369.
- Wang, G., Shen, X., Horvat, J., et al., *J. Phys. Chem.*, 2009, vol. 113, no. 11, p. 4357.
- Jogade, S.M., Sutrave, D.S., and Gothe, S.D., *Intern. J. Adv. Res. Phys. Sci.*, 2015, vol. 2, no. 10, p. 36.
- Li, W., Xu, L., and Chen, J., *Adv. Funct. Mater.*, 2005, vol. 15, p. 851.
- Koza, J.A., He, Z., Miller, A.S., and Switzer, J.A., *Chem. Mater.*, 2012, vol. 24, p. 3567.
- Liu, C., Liu, Q., Bai, L., et al., *J. Mol. Catal. A*, 2013, vol. 70, p. 1.
- Matea, V.R., Shiraib, M., and Rodea, C.V., *Catal. Commun.*, 2013, vol. 33, p. 66.
- Sun, C., Su, X.T., Xiao, F., et al., *Sens. Actuators, B*, 2011, vol. 157, p. 681.
- Tan, J., Dun, M., Li, L., et al., *Sens. Actuators, B*, 2017, vol. 249, p. 44.
- Tan, W., Tan, J., Li, L., et al., *Sens. Actuators, B*, 2017, vol. 249, p. 66.
- Zhou, T., Zhang, T., Deng, J., et al., *Sens. Actuators, B*, 2017, vol. 242, p. 369.
- Vetter, S., Haffer, S., Wagner, T., et al., *Sens. Actuators, B*, 2015, vol. 206, p. 133.
- Jung, D., Han, M., and Lee, G.S., *Sens. Actuators, B*, 2014, vol. 204, p. 596.
- Li, Z., Lin, Z., Wang, N., et al., *Sens. Actuators, B*, 2016, vol. 235, p. 222. <https://doi.org/10.1016/j.snb.2016.05.063>
- Navale, S.T., Liu, C., Gaikar, P., et al., *Sens. Actuators, B*, 2017, vol. 245, p. 524. <https://doi.org/10.1016/j.snb.2017.01.195>
- Fort, A., Panzardi, E., Vignoli, V., et al., *Sensors*, 2019, vol. 19, p. 760.
- Yang, H., Ouyang, J., and Tang, A., *J. Phys. Chem. B*, 2007, vol. 111, p. 8006.
- Qi, Q., Chen, Y., Wang, L., et al., *Nanotechnology*, 2016, vol. 27, p. 1.
- Nam, H.-J., Sasaki, T., and Koshizaki, N., *J. Phys. Chem. B*, 2006, vol. 110, p. 23081.
- Metody polucheniya khimicheskikh reaktivov i preparatov* (Methods for the Preparation of Chemicals), Moscow: IREA, 1971, vol. 23, p. 150.
- Sheldrick, G.M., *Acta Crystallogr., Sect. A: Cryst. Adv.*, 2015, vol. 71, p. 3.
- Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., et al., *J. Appl. Crystallogr.*, 2009, vol. 42, p. 339.
- Alvarez, S., Avnir, D., Llunell, M., and Pinsky, M., *New J. Chem.*, 2002, vol. 26, p. 996.

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