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Influence of the Eliminated Ligand Structure on the Reduction Rate of the Cobalt(III) Complexes

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Abstract—The reduction of the heteroleptic cobalt(III) complexes with bipyridine ligands of different structures of the model drug molecule is studied by in situ NMR spectroscopy. The nature of the ligand eliminated during reduction is shown to exert a substantial effect on the reduction rate, which indicates that an optimum amount of cobalt should be chosen for the redox-activated delivery of a certain drug.

Keywords: in situ nuclear magnetic resonance spectroscopy, dihydroxycoumarin, pyrocatechol, cobalt complexes, redox-activated drug delivery

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INTRODUCTION

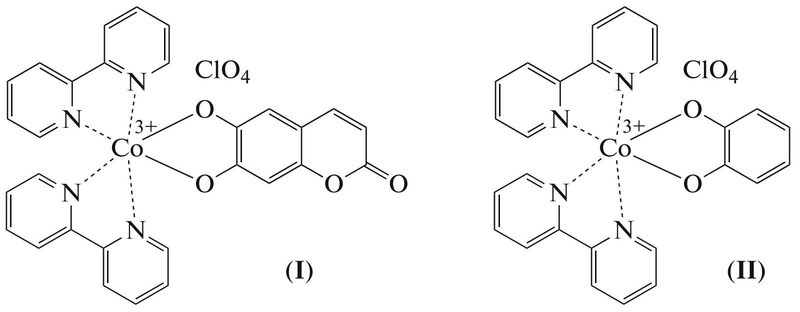
The concentrations of biogenic reducing agents, such as reduced nicotinamide adenine dinucleotide phosphate (NADPH) or glutathione and ascorbate, increases under hypoxia conditions in tissues of so-called solid tumors [1]. These tumors are resistant to chemo- and radiotherapy because of a low oxygen concentration and an elevated level of reducing agents [2]. However, the differentiation of struck with cancer and healthy tissues by the oxygen level made it possible to develop a strategy for redox-activated drugs based on the cobalt(III) complexes selectively affecting tumor cells [3].

The cobalt(III) ion can coordinate and inactivate cytotoxic ligands to form inert complexes that can circulate in the human organism via blood vessels without damaging healthy tissues. However, when getting in tumor cells with an increased content of reducing agents and a low oxygen level, the cobalt(III) complexes are reduced to the corresponding cobalt(II) complexes with dissociation resulting in the release of the drug acted as an organic ligand. The selectivity of the effect of this drug in tissues with a low oxygen level is provided by the fast back oxidation of the cobalt(II) ion to cobalt(III) in healthy tissues with the normal oxygen concentration [4]. A series of the cobalt(III) complexes with some drugs and their precursors of the class of alkylating anticancer remedies, which are analogs of nitrogen mustard [5, 6], a matrix metalloproteinase inhibitor of a wide range of action (marimastat) [7], epidermal growth factor inhibitors [8], esculetin (coumarin derivative with potential anticancer activity) [9], and phenylalanine (which is a model compound of anticancer drug melphalan), have been synthesized to date [10].

Numerous restrictions should be surmounted to transit the developed redox activation strategy to the stage of clinic assays. One of the main problems is that many results obtained in vitro were not reproduced in vivo. This makes it possible to further optimize the properties of the cobalt complexes for using as a molecular platform for redox-activated drug delivery. In addition, the majority of studies in this area is devoted to the choice of ligands for the design of the redox-active cobalt complexes. However, the influence of the structures of the released components themselves on their release was not studied, although this can be an important factor for choosing an optimum platform for delivery. In addition, the released molecules can be reducing agents themselves with respect to the cobalt complexes and can accelerate the reduction.

We have previously proposed the approach that makes it possible to monitor the redox-activation of drugs in the cobalt(III) complexes in situ using NMR spectroscopy. This allowed us to study the reduction with ascorbic acid of the heteroleptic cobalt(III) complexes bearing 2,2'-bipyridine or 1,10-phenanthroline and 2-oxo-2*H*-chromene-6,7-diolate dianion as the ligands [11] and to find that the complex with phenanthroline is reduced much more rapidly.

In this work we used the proposed approach to study the dependence of the rate of the redox-activated release of the model drugs by the cobalt complexes on the molecular structure of the released drugs. The redox-active cobalt(III) complexes [Co(Bipy)$_2$(coumarin-diolate)]ClO$_4$ (**I**) and [Co(Bipy)$_2$(catecholate)]ClO$_4$ (**II**) containing bipyridine and 2-oxo-2*H*-chromene-6,7-diolate or catecholate dianion as ligands (Scheme 1) were chosen as objects of the study [9, 12]. Complex **I** was chosen due to its promising biological properties. For example, the cytotoxicity of complex **I** against colon cancer cells under hypoxia conditions was demonstrated [9]. Complex **II** was chosen for convenience of comparison. Pyrocatechol, whose dianion is a component of complex **II**, contains the structural fragment similar to the fragment in 6,7-dihydroxycoumarin. In addition, the pyrocatechol fragment is a component of many biologically active preparations: antioxidants, adrenalin, and others.



[Co(Bipy)$_2$(coumarin-diolate)]ClO$_4$ [Co(Bipy)$_2$(catecholate)]ClO$_4$

Scheme 1.

EXPERIMENTAL

Complexes **I** and **II** were synthesized according to published procedures [9, 12]. The cobalt(III) complex [Co(Bipy)$_2$Cl$_2$]Cl synthesized by the oxidation of the corresponding cobalt(II) complex with gaseous chlorine [13] was used as the precursor. Dichlorine was prepared by the reaction of potassium permanganate with concentrated hydrochloric acid and dried by passing through concentrated sulfuric acid [14]. 2,2'-Bipyridine (99%, Sigma-Aldrich), cobalt(II) chloride (II) (98%, anhydrous, Sigma-Aldrich), 6,7-dihydroxycoumarin (98%, Sigma-Aldrich), pyrocatechol (99%, Sigma-Aldrich), lithium perchlorate (98%, Alfa Aesar), and triethylamine (99%, Sigma-Aldrich) were used as received.

General procedure for the synthesis of complexes [Co(Bipy)$_2$(coumarin-diolate)]ClO$_4$ (I) and [Co(Bipy)$_2$(catecholate)]ClO$_4$ (II). A solution of triethylamine (1 mmol, 101.2 mg, 139 μL) and the corresponding dihydroxy compound (6,7-dihydroxycoumarin (0.5 mmol, 89 mg) or pyrocatechol (0.5 mmol, 55 mg)) in methanol (10 mL) was added to a solution of [Co(Bipy)$_2$Cl$_2$]Cl (0.5 mmol, 221.1 mg) in methanol (15 mL). The resulting mixture was refluxed for 3 h and then cooled to room temperature. A solution of lithium perchlorate (1.25 mmol, 133 mg) in methanol (5 mL) was added to the mixture, and the resulting mixture was stirred for 30 min on cooling in a water bath for the crystallization of the target complexes. The formed green precipitate was filtered off, washed with isopropanol and diethyl ether, and dried under reduced pressure.

Complex **I**. The yield was 258 mg (80%). ^{1}H NMR (300 MHz; D$_2$O; δ, ppm): 5.92 (d, *J* = 9.3 Hz, 1H, CHC$\underline{H}$COO), 6.50 (s, 1H, C$\underline{H}$), 6.70 (s, 1H, C$\underline{H}$), 7.42–7.45 (m, 4H, C$\underline{H}$), 7.61 (d, *J* = 9.4 Hz, 1H, C$\underline{H}$CHCOO), 7.74–7.80 (m, 2H, C$\underline{H}$), 8.19–8.25 (m, 2H, C$\underline{H}$), 8.36–8.42 (m, 2H, C$\underline{H}$), 8.52 (d, *J* = 8.0 Hz, 2H, C$\underline{H}$), 8.62 (d, *J* = 8.1 Hz, 2H, C$\underline{H}$), 8.69 (d, *J* = 5.7 Hz, 1H, C$\underline{H}$), 8.76 (d, *J* = 5.7 Hz, 1H, C$\underline{H}$). MS (ESI), *m/z*: [Co(Bipy)$_2$(coumarin-diolate)]$^+$, calculated 547.08, found 547.1.

Complex **II**. The yield was 269 mg (93%). ^{1}H NMR (400 MHz; CD$_3$CN; δ, ppm): 6.23–6.27 (m, 2H, C$\underline{H}$), 6.43–6.47 (m, 2H, C$\underline{H}$), 7.44–7.49 (m, 4H, C$\underline{H}$), 7.83 (t, *J* = 6.6 Hz, 2H, C$\underline{H}$), 8.21 (t, *J* = 7.7 Hz, 2H, C$\underline{H}$), 8.57 (d, *J* = 8.0 Hz, 2H, C$\underline{H}$), 8.64 (d, *J* = 8.0 Hz, 2H, C$\underline{H}$), 8.88 (d, *J* = 5.5 Hz, 2H, C$\underline{H}$). MS (ESI), *m/z*: [Co(Bipy)$_2$(catecholate)]$^+$, calculated 479.1, found 479.2.

^{1}H NMR spectra of the cobalt complexes were recorded for solutions in deuterated acetonitrile and water using Bruker Avance 300 and Bruker Avance 400 NMR spectrometers with working frequencies for protons of 300.15 and 400.13 MHz, respectively. Chemical shifts were determined relative to signals of residual protons of the solvents (^{1}H 1.94 ppm for acetonitrile-d$_3$; ^{1}H 4.79 ppm for D$_2$O).

Mass spectrometric analysis of the cobalt complexes and their reduction products was conducted

Table 1. Crystallographic data and experimental and structure refinement parameters for compound **II**

Parameter	Value
Empirical formula	$C_{26}H_{20}N_4O_6ClCo$
FW	578.8
T, K	100
Crystal system	Monoclinic
Space group	*C*2/*c*
Z	4
a, Å	11.9072(3)
b, Å	14.1760(3)
c, Å	14.7894(3)
α, deg	90
β, deg	105.3100(10)
γ, deg	90
V, Å^3	2407.80(9)
ρ_{calc}, g cm^{-3}	1.597
μ, cm^{-1}	8.76
F(000)	1184
$2\theta_{max}$, deg	58
Number of measured reflections	15754
Number of independent reflections	3188
Number of reflections with $I > 3\sigma(I)$	3026
Number of refined parameters	194
R_1	0.0379
wR_2	0.0999
GOOF	1.237
Residual electron density (d_{max}/d_{min}), e Å^{-3}	0.846/–0.639

using an LCMS-2020 liquid chromatograph coupled with mass spectrometer (Shimadzu, Japan) with electrospray ionization and a quadrupole detector (detection of positive and negative ions with *m*/*z* 50–2000). The electrospray voltage was 4.5 kV, and the temperatures of the desolvation line and heating block were 250 and 400°C, respectively. Nitrogen (99.5%) served as the spraying and drying gas, and acetonitrile (99.9+%, Chem-Lab) with a flow rate of 0.4 mL/min was used as the mobile phase. The volume of the analyzed sample was 0.5 μL.

XRD of single crystals of complex **II** was carried out on a Bruker Quest D8 CMOS diffractometer (MoK_α radiation, graphite monochromator, ω scan mode) at $T = 100$ K. The structure was solved using the ShelXT software [15] and refined by full-matrix least squares using the Olex2 program [16] in the anisotropic approximation for F^2_{hkl}. Positions of hydrogen atoms were calculated geometrically and refined in the isotropic approximation by the riding model. The main crystallographic data and refinement parameters are given in Table 1.

The crystallographic parameters for complex **II** were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 2262269; http://www.ccdc.cam.ac.uk/).

In situ NMR spectroscopy. The corresponding cobalt complex **I** (6.4 mg) or **II** (5.8 mg), ascorbic acid (20 μmol, 3.6 mg), CD_3CN (550 μL), and dibromomethane as the internal standard (3 μL) were placed in an NMR tube with a screw top and septa. Then the tube was frozen in liquid nitrogen and filled with argon.

The ^{1}H NMR spectrum of the initial mixture was recorded at 40°C on a Bruker Avance 300 spectrometer with a proton working frequency of 300.15 MHz. Chemical shifts (δ, ppm) were determined relative to the residual signal of the solvent (^{1}H 1.94 ppm for CD_3CN). The following detection parameters were used: spectral range 150 ppm, detection time 0.2 s, relaxation delay time 0.6 s, pulse duration 9.5 μs, and

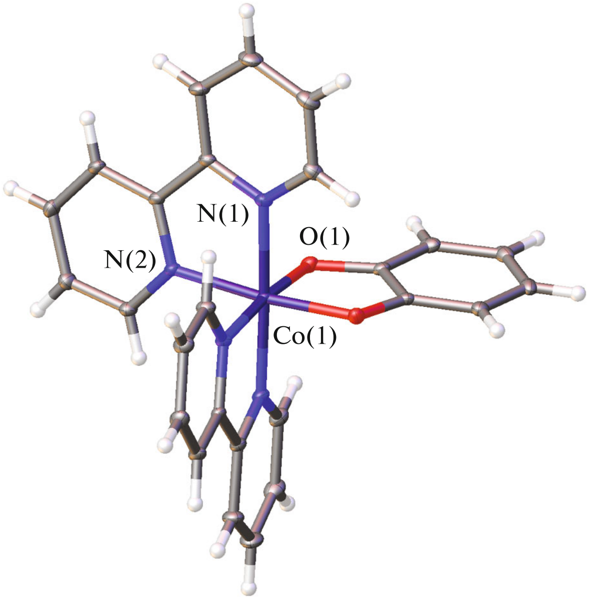


Fig. 1. General view of complex **II** illustrating the coordination environment of the cobalt(III) ion. Hereinafter perchlorate anions are omitted and non-hydrogen atoms are shown as thermal vibration ellipsoids ($p = 30\%$). Numeration is presented only for the metal ion and symmetrically independent heteroatoms.

acquisition number 32. The obtained free induction decays were processed to increase the signal/noise ratio by exponential weighing with the coefficient to 1. Then D_2O (150 μL) was syringed through the septa, and the mixture was shaken until the complete dissolution of ascorbic acid. The NMR spectra were further recorded at an interval of 2 min within 40 min at 40°C using the same parameters as those for the detection of the spectrum of the initial mixture. The conversion rate was estimated from the consumption of the initial complex. The content of the complex in the mixture (in % of the initial amount) was calculated from the ratio of the integral intensity of the signal from the dibromomethane protons (5.09 ppm) to the integral intensity of the doublets with chemical shifts of 8.84 ppm for complex **I** and 8.88 ppm for complex **II** chosen because of convenience of integration, since they were observed during the whole reduction and were not overlapped with other signals.

RESULTS AND DISCUSSION

The chosen cobalt(III) complexes $[Co(Bipy)_2(coumarin\text{-}diolate)]ClO_4$ (**I**) and $[Co(Bipy)_2(catecholate)]ClO_4$ (**II**) were synthesized using previously described procedures [9, 12] by the reactions of $[Co(Bipy)_2Cl_2]Cl$ with 6,7-dihydroxycoumarin and pyrocatechol, respectively, in the presence of triethylamine and lithium perchlorate. The complexes were isolated in the individual form and characterized by mass spectrometry and NMR spectroscopy. The structure of complex **II** was also confirmed by XRD (Fig. 1). According to thus obtained data, the cobalt(III) ion, which occupies the partial position in the crystal (twofold axis passing through the metal ion and the O...O line center of the catecholate dianion), exists in the low-spin state, which is unambiguously indicated by the bond lengths Co–N < 1.95 Å [17]. Its coordination environment formed by four nitrogen atoms of two symmetrically equivalent bipyridine ligands (Co–N 1.9323(14) and 1.9452(14) Å) and two symmetrically equivalent oxygen atoms of the catecholate dianion (Co–O 1.8804(12) Å) has a shape close to an octahedron. This can quantitatively be confirmed by "symmetry measures" [18] that describe the deviation of the coordination polyhedron CoX_6 (X = O, N) from an ideal octahedron. The lower this value, the better the description of the polyhedron shape by the corresponding polygon. In complex **II**, the corresponding value estimated from the XRD data using the Shape 2.1 program [18] is only 0.365. For comparison, the symmetry measure describing the deviation of the coordination polyhedron from an ideal trigonal prism takes a noticeably higher value of 14.913. The symmetrically equivalent bipyridine ligands in the crystal of this complex form a stacking interaction with the distance between the centroids of the pyridine rings and angle between them equal to 3.3986(17) and 3.4713(17) Å and 3.90(6)°, respectively, joining the $[Co(Bipy)_2(catecholate)]^+$ cations into 1D chains along the crystallographic *c* axis (Fig. 2).

The reduction of cobalt(III) complexes **I** and **II** were studied in situ by NMR spectroscopy using the earlier developed approach [11] with minor modifications. The tube with a screw top and septa containing a solution of the corresponding complex in acetonitrile-d_3 with 2 equivalents of ascorbic acid and 3 μL of dibromomethane acting as the internal standard was frozen in liquid nitrogen, evacuated, and filled with argon. The ^1H NMR spectrum of the resulting mixture was recorded at 40°C. Then deuterated water was added through the septa into the tube to dissolve ascorbic acid followed by ^1H NMR spectra recording at 40°C.

The reduction of the heteroleptic cobalt(III) complexes (Scheme 2) resulted in the isostructural cobalt(II) complexes, which rapidly eliminated the 2-oxo-2*H*-chromene-6,7-diolate or catecholate dianion accompanied by the formation of the cobalt(II) complex $[Co(Bipy)_2(Solv)_2]^{2+}$. In the solution, the latter entered into the exchange reaction of the ligands with analogous complex ions with the formation of the $[Co(Bipy)_3]^{2+}$ complex and solvated cobalt ions [9, 11].

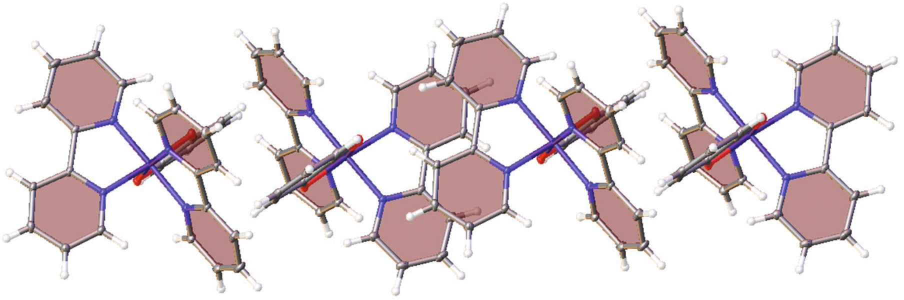
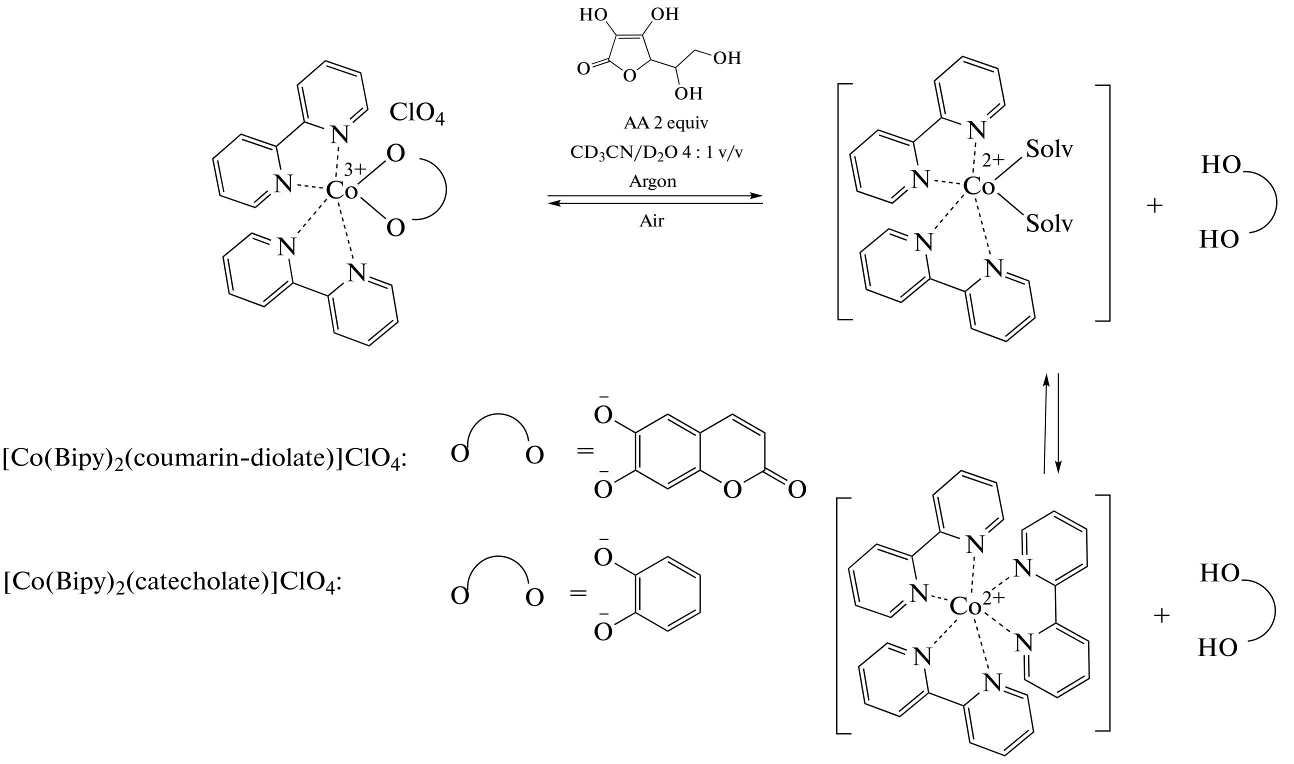


Fig. 2. Fragment of the crystal packing of complex **II** illustrating the formation of 1D chains due to the stacking interaction between the bipyridine ligands (emphasized by pink color).



Scheme 2.

The ^{1}H NMR spectra illustrating the dynamics of the reduction of complex **II** with ascorbic acid in an argon atmosphere are shown in Fig. 3. This process resulted in the formation of the complexes bearing the paramagnetic Co^{2+} ion and, hence, the diamagnetic (from 0 to 10 ppm) and paramagnetic (from 15 to 120 ppm) ranges can be distinguished in the ^{1}H NMR spectra. The first range contained signals of the initial complex, ascorbic acid, its oxidation product, and free pyrocatechol. The second range exhibits the signals of the formed cobalt(II) complexes. It is seen that the signal intensity in the diamagnetic range decreases and that in the paramagnetic range, on the contrary, increases as the reaction occurs. The number of observed signals in the paramagnetic spectral range remained unchanged during reduction, and only their relative intensity changed. Note that the paramagnetic ranges of the NMR spectra detected 40 min after the initiation of the reduction of cobalt(III) complexes **I** and **II** contained eight signals, whose chemical shifts coincided (Fig. 4). Three additional signals with a low intensity were observed in the spectrum of the reduction products of complex **II**. However, the same signals appeared in the spectra of a mixture of complex **I** with ascorbic acid several hours after the reaction onset. The coincidence of the chemical shifts for the signals in the paramagnetic range indicated that the cobalt(II) complexes $[Co(Bipy)_2(L)]^{2+}A_2^-$ (where L is

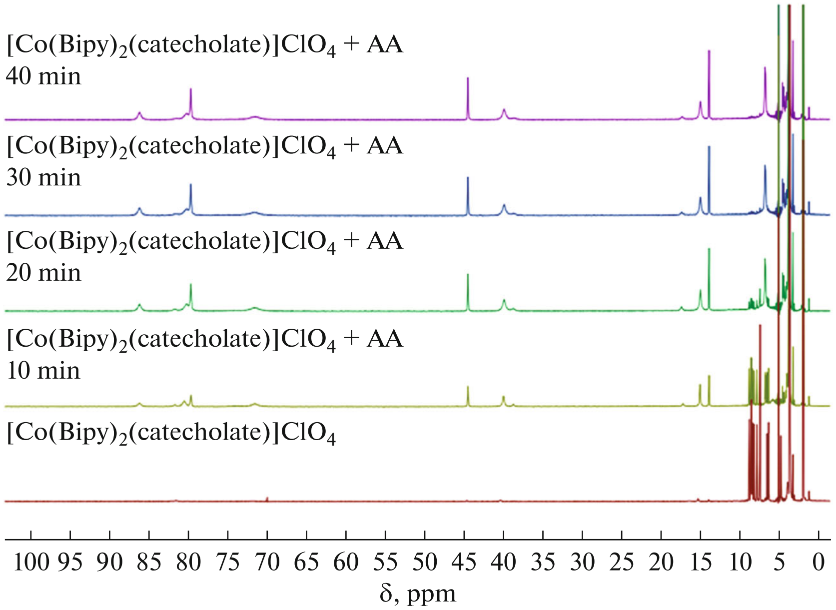


Fig. 3. Dynamics of changing the ^{1}H NMR spectrum with time for the reduction of complex **II** with ascorbic acid in argon (the spectrum was detected in a mixture of acetonitrile-d$_3$ and deuterated water (4 : 1, vol/vol)).

the 2-oxo-2*H*-chromene-6,7-diolate or catecholate dianion, and A$^-$ is the counterion) were not accumulated in the reaction mixture. A comparison of the detected spectra with the spectrum of the cobalt(III) complex [Co(Bipy)$_3$](ClO$_4$)$_2$ recorded in acetonitrile-d$_3$ shows that the most intense signals coincide with the signals in the spectrum of the indicated complex (Fig. 4, marked with *). An analysis of the obtained data suggests that the reduction of cobalt(III) complexes **I** and **II** with ascorbic acid is accompanied by the formation of the cobalt(II) complex [Co(Bipy)$_3$]-(ClO$_4$)$_2$ as the major product. The mass spectra of the reaction mixtures (Fig. 5) contain the signals corresponding to the initial complex ions [Co(Bipy)$_2$(L)]$^+$ and also signals with *m/z* 263.6, 405.9, and 470.2 attributed to ions [Co(Bipy)$_3$]$^{2+}$, [Co(Bipy)$_2$Cl]$^+$, [Co(Bipy)$_2$(ClO$_4$)]$^+$. The appearance of signals of the adducts with the chloride anion can be due to the incomplete replacement of the chloride ion by perchlorate during the synthesis of the studied complexes from [Co(Bipy)$_2$Cl$_2$]Cl. The NMR spectroscopy and mass spectrometry data confirm the reduction mechanism shown in Scheme 2.

In addition to the information on the composition of the reaction mixture formed upon the reduction of cobalt(III) complexes **I** and **II** with ascorbic acid in an argon atmosphere, an analysis of the data of in situ NMR spectroscopy made it possible to compare the reaction rates for two complexes and to determine the reaction order and rate constant. The kinetic curves of consumption of complexes **I** and **II** during their reduction with ascorbic acid in an argon atmosphere are compared in Fig. 6. Figure 6 shows that the complex containing the catecholate dianion is reduced by ~2 times more rapidly. The half-life times for complexes **II** and **I** were 9 and 19 min, respectively. The time dependences of the logarithm of the concentrations of the initial complexes were approximated by a straight line with the reliability coefficient close to unity (Fig. 7). The linear approximation indicated the first order with respect to the initial reagent for the reduction of the studied complexes. The reduction rate constant for cobalt(III) complexes **II** and **I** with ascorbic acid in an inert atmosphere at 40°C was estimated from the slope ratios of the lines shown in Fig. 7 and was equal to 2.0×10^{-3} and 1.2×10^{-3} s^{-1}, respectively. An increase in the reduction rate of the complexes upon the replacement of 6,7-dihydroxycoumarin by pyrocatechol can be related to a decrease in the electron density on the cobalt ion due to a decrease in the size of the conjugated π system on going from 6,7-dihydroxycoumarin to pyrocatechol.

Thus, we studied the reduction of cobalt(III) complexes **II** and **I** differed only by the ligand acting as the model drug by in situ NMR spectroscopy. Complex **II** bearing the catecholate dianion was shown to be reduced with ascorbic acid by ~2 times more rapidly than the complex containing the 2-oxo-2*H*-chromene-6,7-diolate dianion. The reduction rate constants were determined. The dependence of the redox-activation rate of the cobalt complex on the structure of the model drug as the component of the complex indicates that the molecular design of an

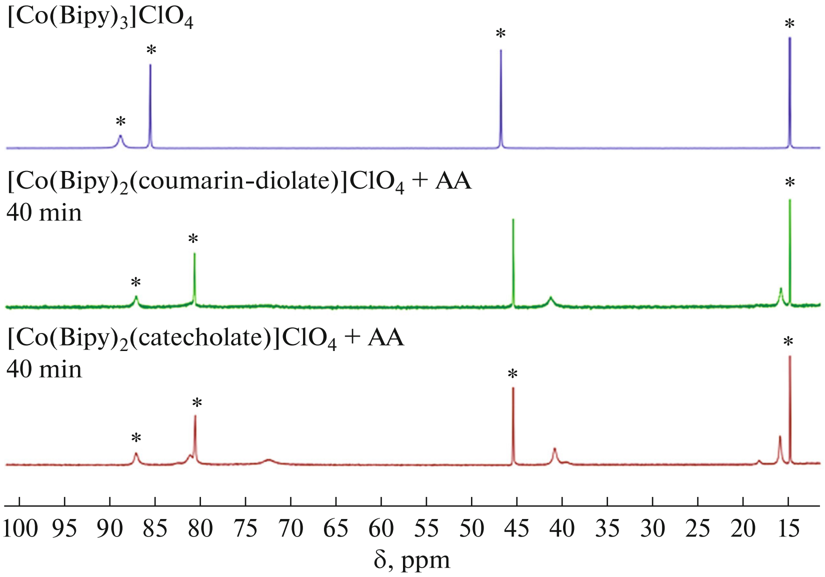


Fig. 4. Comparison of the paramagnetic ranges of the NMR spectra of the complex $[Co(Bipy)_3]ClO_4$ (top) and the reduction products of complexes **I** (center) and **II** (bottom).

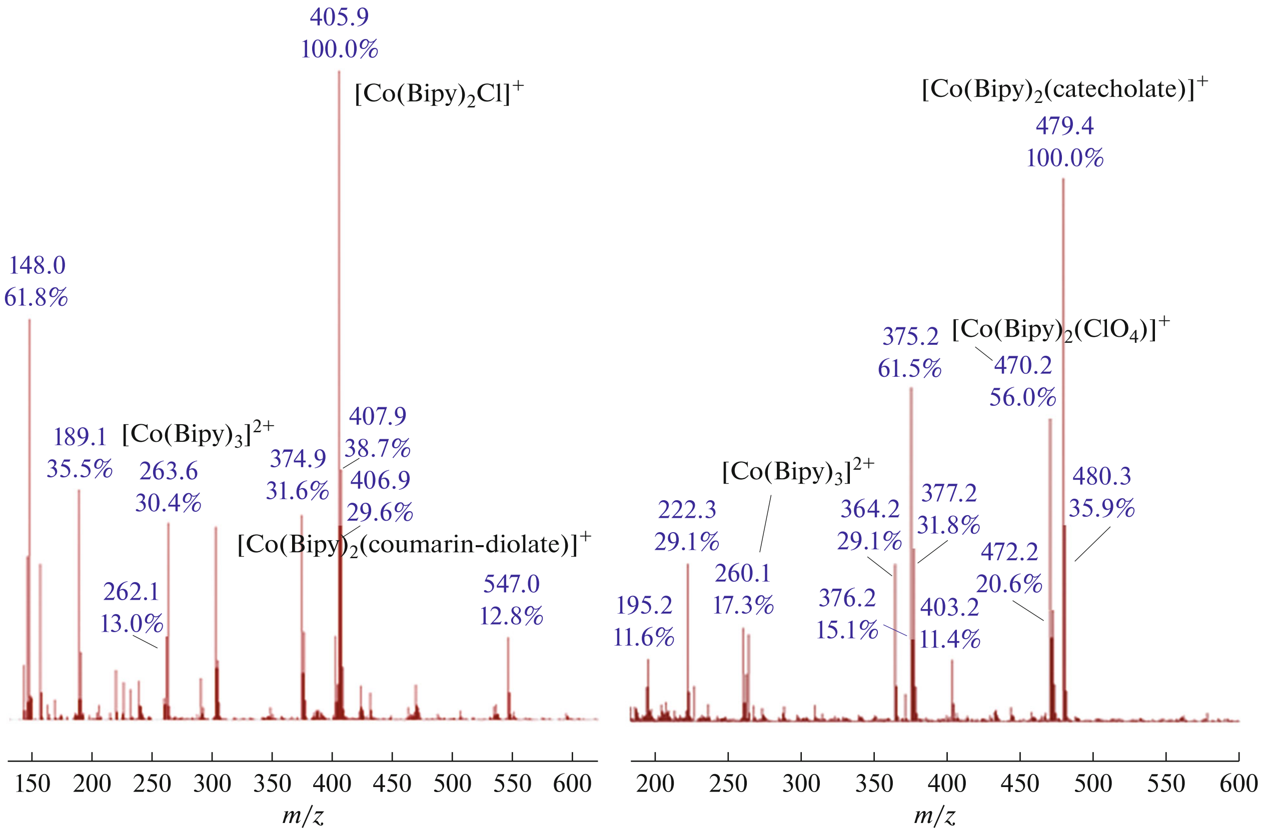


Fig. 5. Comparison of the mass spectra of the reduction products of complexes **I** (left) and **II** (right).

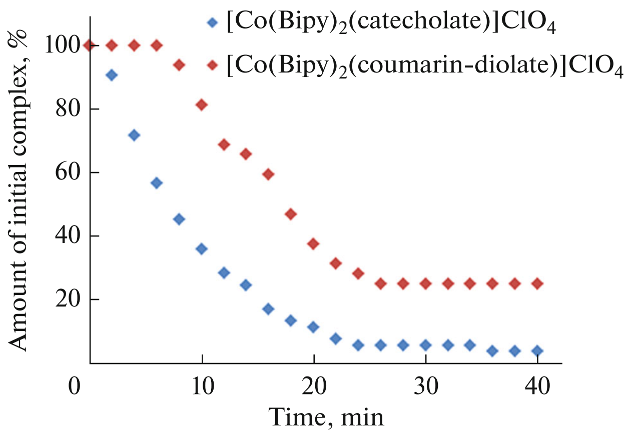


Fig. 6. Kinetic curves of consumption of complexes **I** and **II** for the reduction with ascorbic acid in an argon atmosphere.

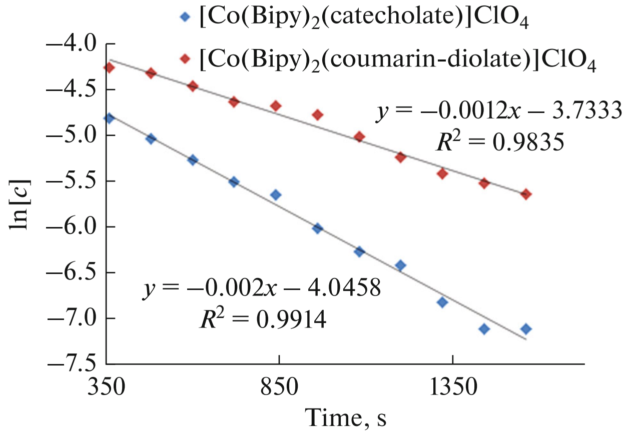


Fig. 7. Logarithms of the concentration ln[*c*] for complexes **I** and **II** vs. reaction time for the reduction with ascorbic acid in an argon atmosphere.

optimum complex is necessary for the targeted delivery of a certain drug.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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