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Catalase Activity of Cobalt(II) Complexes with *N,N,N′,N′*-Tetrasubstituted Thiocarbamoylsulfenamides

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Abstract—On the base of the kinetic and activation parameters of the hydrogen peroxide decomposition in the presence of chelates of CoX_2 salts (X = Cl, Br, I, NCS) with *N,N,N′,N′*-tetrasubstituted thiocarbamoylsulfenamides containing exocyclic (out-of-chelate) fragments of dimethylamine (**I**), piperidine (**II**), and piperazine (**III**) the nature of acido-ligands influence on catalase activity of complexes **I–III** was revealed, depending on the structure and composition of the chelating ligand. Mononuclear complexes **I**(Br) and **II**(Br) can transform into 10-membered binuclear macrochelate intermediates .

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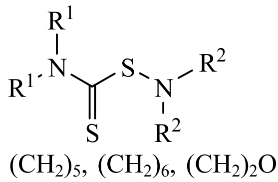
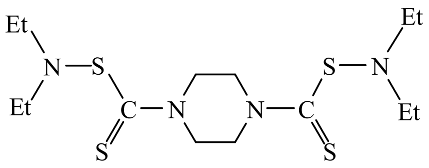
The intensive development of the chemistry of coordination compounds based on the N- and S-chelating ligands has stimulated the interest of researchers to the preparation of new related polydentate systems and complexes. A large number of cobalt(II), copper(II), and zinc(II) complexes containing chelated sites of the $\overset{\frown}{\text{N–M–S}}$ type were synthesized. This corresponds, above all, to the complexes of transition metals with various derivatives of dithiocarbamic acids, which, due to the unique properties, proved to be interesting targets for the development of stereochemical concepts and are widely used in the rubber curing, in the chemistry and technology of elastomers, in organic synthesis, analytical chemistry, medicine, biology, engineering, agriculture, etc. [1–3]. However, complexes of dithiocarbamides (thiocarbamoylsulfenamides), practically have not been studied, probably due to a significant instability of the thiocarbamoylsulfenamides [2, 4–7] owing to a specific structure of the sulfenamide groups. However, this difficulty probably can be circumvent by binding (coordination) thiocarbamoylsulfenamide with a metal center, since it is known [8] that this changes dramatically the structure and reactivity of the corresponding ligand. Thus, a number of N- and S-containing ligand systems and their metal complexes can be significantly expanded by inclusion of thiocarbamoylsulfenamides, thus increasing a variety of compounds appropriate for creation of new and effective rubber curing accelerators, catalysts, biologically active substances, etc.

Following this conception, the authors of [9–17] were first investigated the complexes of cobalt(II), copper(II) and zinc(II) with thiocarbamoylsulfenamides, the general formula of which is shown below .

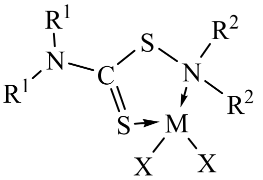


R^1 = Me, Et; $(R^1)_2 = (CH_2)_5, (CH_2)_6, (CH_2)_2O(CH_2)_2$; R^2 = Me, $(R^2)_2 = (CH_2)_5$.

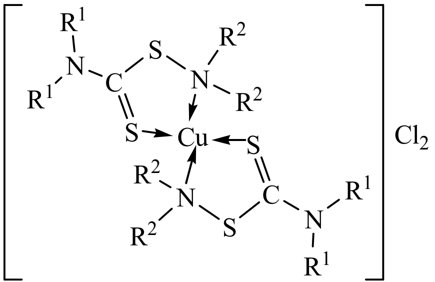
These ligands (L) were obtained [9, 10] in up to 94% yields by the oxidative condensation of the corresponding sodium dithiocarbamates with secondary amines in the presence of iodine. When disodium piperazine-*N,N*-bisdithiocarbamate interacted in the same conditions with diethylamine 1,4-piperazinebiscarbothiosulfenediethylamide was isolated in 74% yield [11].



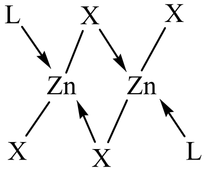
The techniques of synthesis was developed and more than 40 new coordination compounds of thiocarbamoylsulfenamides with the salts MX_2 (M = Co, Zn, X = Cl, Br, I, NCS; M = Cu, X = Cl) were identified. Based on the data of elemental analysis, X-ray phase analysis, mass spectrometry, IR, ^1H NMR, ESR, and electron spectroscopy, and conductometry, magneto-chemistry and XRD (in the case of Zn complexes) conclusions were made on the mode of coordination of the ligands in the obtained complexes and the structure of the coordination polyhedra in dependence on the nature of the metal, ligand and the anion X [9, 11–15]. It was shown that in mixed organic solvents metal complexes of various types are formed, and the molar ratio of M:L may be 1:1 or 1:2 with bidentate coordination of L through the thione sulfur atoms and the nitrogen atoms of sulfenamide (five-membered chelate metallocycle), and also 2:1.



LMX_2



$[L_2Cu]Cl_2$



$L_2Zn_2X_4$

In the dimeric complexes of Zn(II), with bridging halogen atoms, the monodentate coordination of L is realized through thione sulfur atom. The coordination number of metal-complexing agents equal to four, and the pseudotetrahedral configuration of the metal center is common to all the obtained complexes.

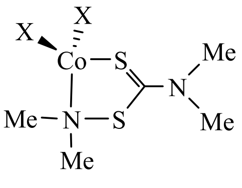
The thermogravimetric study of these complexes showed that they are thermally more stable than the original thiocarbamoylsulfenamides. Also it was revealed that at the temperature of the first exoeffects the thermal decomposition of the $LCoX_2$ complexes leads to the formation of Co(III) and Co(II) compounds.

Some of the synthesized metal complexes were tested as chemical additives in the compositions of sulfur-based curing systems [16]. It was found that the activity of these complexes depended on the structure of the ligands L (containing fragments of dimethylamine, piperidine, or morpholine) and the nature of the metal and the acido-ligands X: bromide complexes of cobalt(II) and zinc(II) were highly active accelerators, while the $LCoBr_2$ complexes proved to be adhesion promoters of rubber to the metal cord. The $LMBr_2$ complexes (M = Co, Zn) were effective catalysts for the process of thermooxidative structuring of oligobutadiene of brand KRASOL LB of various molecular weight [17]. Note that complexes $LCoBr_2$ prove to be true or primary siccatives, and the complexes $LZnBr_2$, promoters [9]. At the same time it was found that, depending on the bacterial strain and exposure time, as well as on the composition of the $LZnH_2$ complexes (X = Cl, Br, NCS), the nature of their influence on elastase and α-L-ramnozidase activity of enzymes changes: these complexes inhibit the first but to the same extent activate the second type of activity [9].

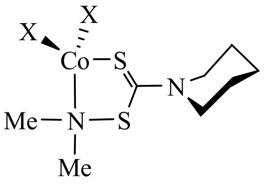
Thus, combining in a single molecule of thiocarbamoylsulfenamide coordination compound a metal cation (Co^{2+}, Cu^{2+}, Zn^{2+}), acido-ligand (Cl^-, Br^-, I^-, NCS^-), mono- and bidentate (chelating) ligands L allow to change the composition and the structure of these complexes and, therefore, vary widely their functional properties.

Note also that the cobalt(II) complexes with dithiocarbamates (similar in structure to the thiocarbamoylsulfenamides) show antialkylating, anti-HIV, anticancer, antifungal, and antimicrobial properties [18]. The latter is very important, because the permanent use of antibiotics, corticosteroids, immunosuppressive agents, cytotoxic drugs etc. led to an increase in systemic infections caused by the relevant bacteria [19]. It is possible that the mono- and binuclear complexes of cobalt(II) with the ligands of type L also have a range of potentially interesting biological properties, and the information about their catalase activity may be useful for understanding the mechanisms of action of metalloenzymes [20, 21] and the design of new drugs based on the thiocarbamoylsulfenamide complexes.

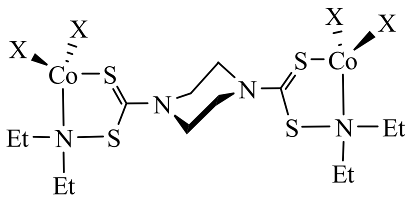
This report describes the features of the kinetics of hydrogen peroxide decomposition in the presence of mono- (**I**, **II**) and binuclear (**III**) complexes of cobalt(II) with thiocarbamoylsulfenamides with composition $CoLX_2$ and Co_2LX_4, and the influence is discussed of the structure of chelating ligands L and the nature of acido-ligands X on the catalytic activity of these complexes.



I



II



III

X = Cl, Br, I, NCS.

The kinetics of hydrogen peroxide decomposition was studied by volumetry as described in [11]. Typical curves of oxygen isolation are shown in Fig. 1. Kinetic and activation parameters of the reactions studied calculated with the known formulas are given in Table 1.

A notable non-catalytic decomposition of H_2O_2 is observed at a temperature above 318 K. Previously it was also found that at 318 K at the initial concentration in the ranges: $[CoX_2]_0$ = $(2\times10^{-2}–1\times10^{-1})$ M and $[H_2O_2]_0$ = (0.24–0.5) M the hydrogen peroxide either almost not decomposed (X = Cl, Br, NCS), or (in the

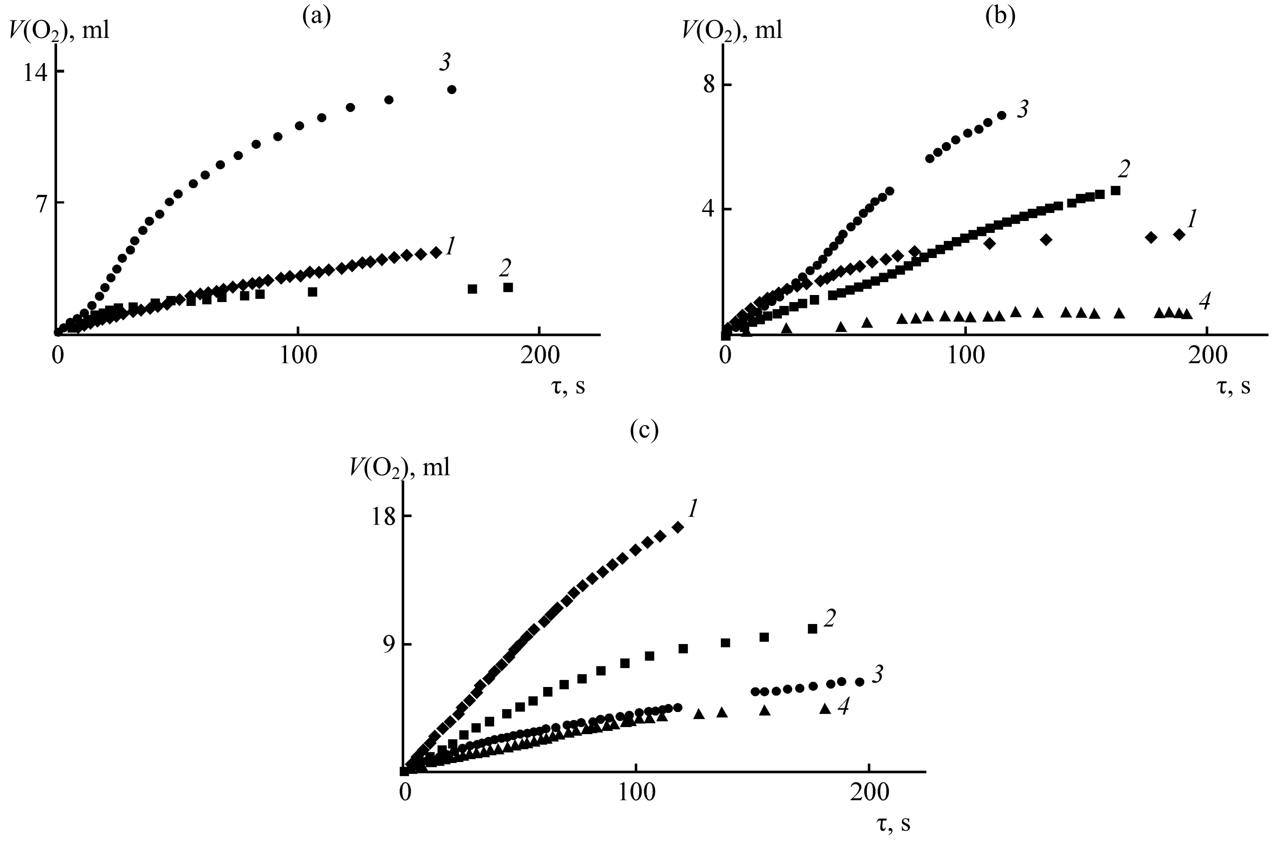


Fig. 1. Examples of kinetic curves of oxygen isolation in hydrogen peroxide decomposition (318 K) in the presence of complex (a) **I**, (b) **II**, and (c) **III**; X = Cl (*1*), Br (*2*), I (*3*), NCS (*4*).

Table 1. Kinetic and activation parameters of hydrogen peroxide decomposition in the presence of complexes **I**, **II**, and **III**[a]

Comp. no.	X	T, K	$W^0\times10^{4\,\mathrm{b}}$, mol l^{-1} s^{-1}	n_{Cat}	n_{H2O2}	$k^{\mathrm{c}}\times10^2$	log $W^{0\,\mathrm{b}}$	$E_{\mathrm{a}}^{\mathrm{eff}}$, kJ mol^{-1}	$\Delta H^{\#}$, kJ mol^{-1}	$-\Delta S^{\#}$, eu	$-T\Delta S^{\#}$, kJ mol^{-1}	$\Delta G^{\#}$, kJ mol^{-1}	$T\Delta S^{\#}$, %
Ia	Cl	308	0.5	0.6±0.2	0.8±0.2	1.6	20.5	78	75	41	13	88	15
		318	1.3			4.3							
		328	3.2			10.3							
Ib	Br	298	0.9	1.1±0.1	0.6±0.1	18.1	7.8	42	40	125	40	80	50
		308	1.6			32.1							
		318	2.9			57.6							
		328	4.3			84.7							
Ic	I	298	0.8	1.1±0.1	0.8±0.1	16.2	19.9	73	70	25	8.0	78	10
		308	1.4			28.9							
		318	6.2			125.3							
		328	9.7			197.2							
Id	NCS	328	0.3	1.1±0.1	0.5±0.1	–	–	–	–	–	–	–	–
IIa	Cl	308	1.3	0.6±0.1	0.4±0.1	0.8	12.2	54	52	118	38	90	42
		318	2.5			1.6							
		328	4.6			2.9							
IIb	Br	308	0.5	1.1±0.1	0.8±0.1	9.6	15.8	66	63	59	19	82	23
		318	1.1			23.9							
		328	2.2			46.1							
IIc	I	308	1.7	0.9±0.1	0.9±0.1	12.3	16.1	64	61	65	21	82	25
		318	2.6			18.6							
		328	7.9			56.6							
IId	NCS	308	0.2	0.5±0.1	0.9±0.1	–	16.5	67	66	63	20	86	23
		318	0.3			2.0							
		328	1.6			10.3							
IIIa	Cl	298	1.3	0.9±0.1	1.1±0.1	12.8	17.6	66	63	50	15	78	19
		308	2.6			26.1							
		318	6.7			68.5							
IIIb	Br	298	1.2	0.8±0.1	1.1±0.1	8.8	7.5	41	38	136	42	80	52
		308	2.1			15.7							
		318	3.3			24.7							

Table 1. (Contd.)

Comp. no.	X	T, K	$W^0\times10^{4\,b}$, mol l^{-1} s^{-1}	n_{Cat}	n_{H2O2}	$k^c\times10^2$	log $W^{0\,b}$	E_a^{eff}, kJ mol^{-1}	$\Delta H^\#$, kJ mol^{-1}	$-\Delta S^\#$, eu	$-T\Delta S^\#$, kJ mol^{-1}	$\Delta G^\#$, kJ mol^{-1}	$T\Delta S^\#$, %
IIIc	I	298	0.9	0.7±0.3	1.1±0.2	4.7	5.6	37	34	156	48	82	58
		308	1.9			10.0							
		318	2.3			12.0							
IIId	NCS	298	0.5	0.8±0.1	0.7±0.2	2.2	6.3	36	34	150	46	84	55
		308	0.9			4.3							
		318	1.3			6.2							

[a] $[H_2O_2]_0$ = (0.05–0.42) M, $[Cat]_0$ = (2.0×10^{-4}–2.0×10^{-3}) M. [b] Initial rate of H_2O_2 decomposition at $[Cat]_0$ = 0.01 M and $[H_2O_2]_0$ = 0.2 M. [c] The constants of different dimensions. Calculated by solving a system of linear equations $\log W^0 = \log k + n_{Cat}\log C_{Cat} + nH_2O_2\log C(H_2O_2)$. [d] Value analogous to the pre-exponential factor of the Arrhenius equation: $\ln W^0 = \ln W^0 - E_a^{eff}/RT$, where E_a^{eff} is effective activation energy (temperature coefficient).

presence of CoI_2) the initial rate of oxygen isolation $W^0 \approx 3.5\times10^{-5}$ M. Thus, we can conclude that the complexes **I**, **II**, and **III**, in contrast to the corresponding salts CoX_2, exhibit catalase activity.

However, as follows from Table. 1, the value of W^0 in the presence of the studied complexes, all other things being equal, vary in the range $W^0_{max}/W^0_{min} \le 20$, which corresponds to the changes in the free energy of activation ($\Delta G^\#$) values calculated from the Eyring equation, $\Delta G^\#_{max} - \Delta G^\#_{min}$ = (12±3) kJ mol^{-1}.

Somewhat surprising is the fact that the nature of the influence of acido-ligands X on the reaction rate to a remarkable extent is determined by the composition and structure of the chelating ligands L.

As show Table 1 and Fig. 2, the series of catalase activity observed for the complexes of **I** (W^0) (NCS < Cl < Br ≤ I), differs from that of the complexes **II** (NCS ≤ Br ≤ Cl ≤ I) and is almost reverse to the complexes **III** (NCS < I < Br < Cl). The thiocyanate complexes were "insensitive" to the nature of the ligand L and exhibit minimal (or comparable at 328 K, see Table 1) activity with the complex **II**(Br) in each of the three reaction series. Note also that (as expected) these series of complexes **I–III** activity is almost reverse to the changes in $\Delta G^\#$ values.

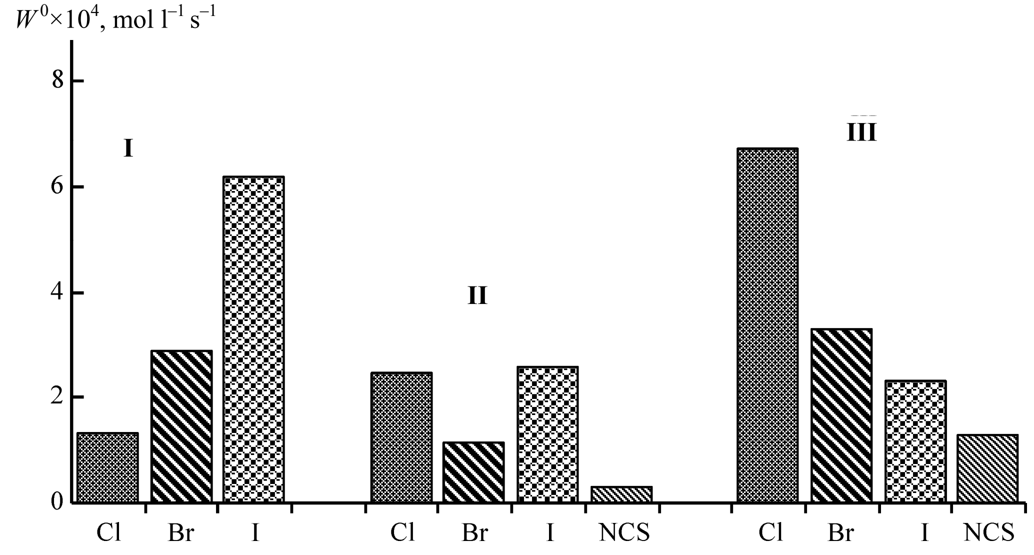


Fig. 2. Effect of acido-ligands X on the initial rate of hydrogen peroxide decomposition (318 K) in the presence of complexes **I, II**, and **III**.

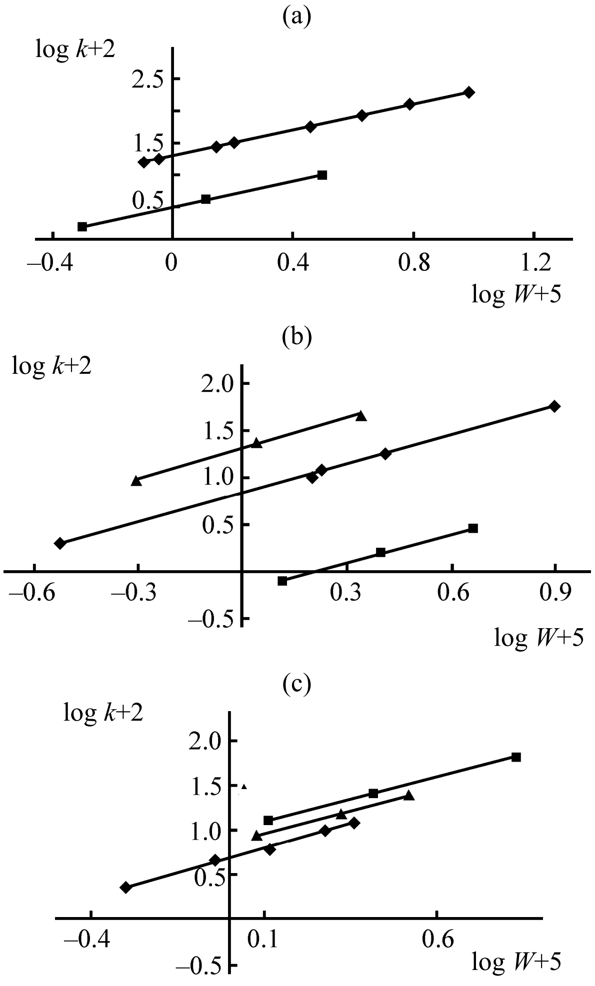


Fig. 3. Comparisons of rate and rate constants of hydrogen peroxide decomposition in the presence of complex **I** (a), **II** (b), and **III** (c) in the coordinates log k – log W^0. See explanation in the text.

Interestingly, the changes in the initial rate of oxygen isolation in the presence of complexes **I–III** (Table 1, 308 K and 318 K) are different despite the same acido-ligands X: **I** < **II** < **III** (X = Cl), **I** > **II** ≈ **III** (X = Br), **I** ≥ **II** ≈ **III** (X = I), and **I** < **II** ≈ **III** (X = NCS).

Thus, we can conclude that, despite the similarity of chelate rings and the ligand environment at the metal centers in complexes **I–III**, their catalase activity is not determined by a single factor. It is possible that these features are due to the character of the tertiary (exocyclic) nitrogen atoms of the corresponding thiocarbamoylsulfenamides not involved in the coordination with the cobalt atom, namely, to the fragments of dimethylamine (**I**), piperidine (**II**), and piperazine (**III**).

According to Table 1 (see footnote b), the data presented in the coordinates log k–log W^0 should be straight lines with a slope equal to one, that is, $\log k = \log W^0 + C$, which is clearly demonstrated by Fig. 3 ($\tan \alpha = 1.03 \pm 0.03$; $1.00 > R^2 > 0.99$). However, in the case of complex **I** (Fig. 3a), the entire set of data points is represented by two families ($\Delta C = 0.8$), one of which corresponds to the chloride complex, and the second, to bromide and iodide. For complex **II** (Fig. 3b) similar dependences are represented by three straight lines corresponding (in descending order of C) to bromide, iodide with thiocyanate ($\Delta C = C_{\max} - C = 0.5$), and chloride ($\Delta C = 1.0$). Qualitatively similar pattern is observed for complexes **III** (Fig. 3c), with the only difference that the family with $C_{\max}$ corresponds to chlorides, and for the bromide and iodide with thiocyanate the ΔC values are 0.13 and 0.31, respectively. Apparently, these three families are closer than in the case of complexes **II**, and the joint family of chloride and bromide complexes **III** is approximated satisfactorily by a straight line $\log k = (1.1 \pm 0.1) \log W^0 + (0.90 \pm 0.06)$ ($R^2 = 0.95$, $N = 6$, $s_y = 0.08$). At the same time, the combining of all three families leads to the worst correlation $\log k = (1.3 \pm 0.1) \log W^0 + (0.75 \pm 0.04)$ ($R^2 = 0.93$, $N = 12$, $s_y = 0.1$) with a coefficient of regression significantly greater than one.

Note also that the behavior of the catalase activity of the complexes in the scale of log k is qualitatively in line with the above (in the W^0 scale) only in the case of complexes **III** (Fig. 3c), which can be explained by proximity (regardless practically of the acido-ligands X nature) of fractional orders (n_{Cat} and n_{H2O2}) to unity (Table 1) and the total reaction order to two.

However, the complexes **I** and **II** (Table 1) are characterized by the fractional reaction order $n < 1$, especially when X = Cl, which indicates the possibility of a significant contribution to the observed rate in such cases of alternative routes and hence this factor should be considered in the analysis of catalase activity of complexes **I–III**. It is logical to expect, for example, that the n_{Cat} values will decrease when catalytic (see below) and non-catalytic (radical [22], $HO^{\bullet} + H_2O_2 \rightarrow H_2O + HOO^{\bullet}$) routes are comparable.

As for the fractional reaction order with respect to hydrogen peroxide (n_{H2O2}), it is clear from the data in Table 1 on the initial concentrations of $[\mathrm{Cat}]_0$ and $[H_2O_2]_0$, even at the highest concentrations of the catalyst and the minimum H_2O_2 the excess of the latter

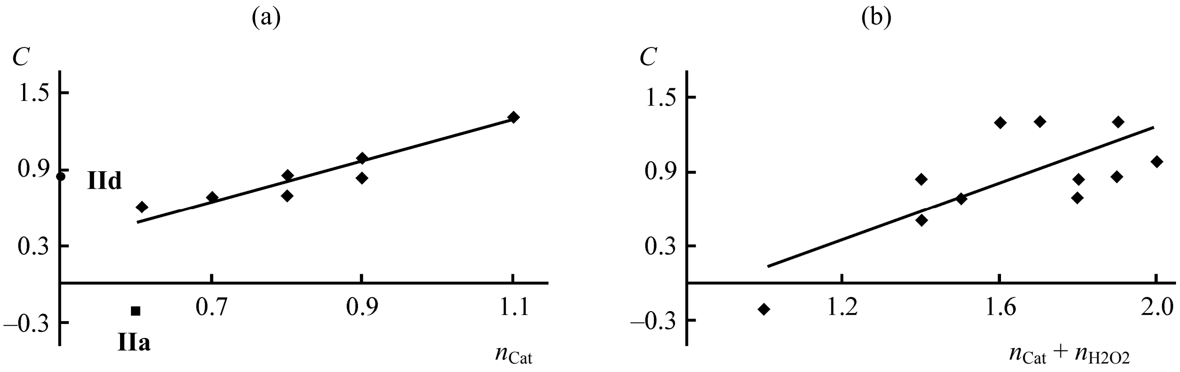


Fig. 4. Comparison of the constant (*C*) dependences log k = log W^0 + *C* (see Fig. 3) with the reaction order in catalyst (a) and the overall reaction order (b) of the rate of hydrogen peroxide decomposition in the presence of complexes **I–III**.

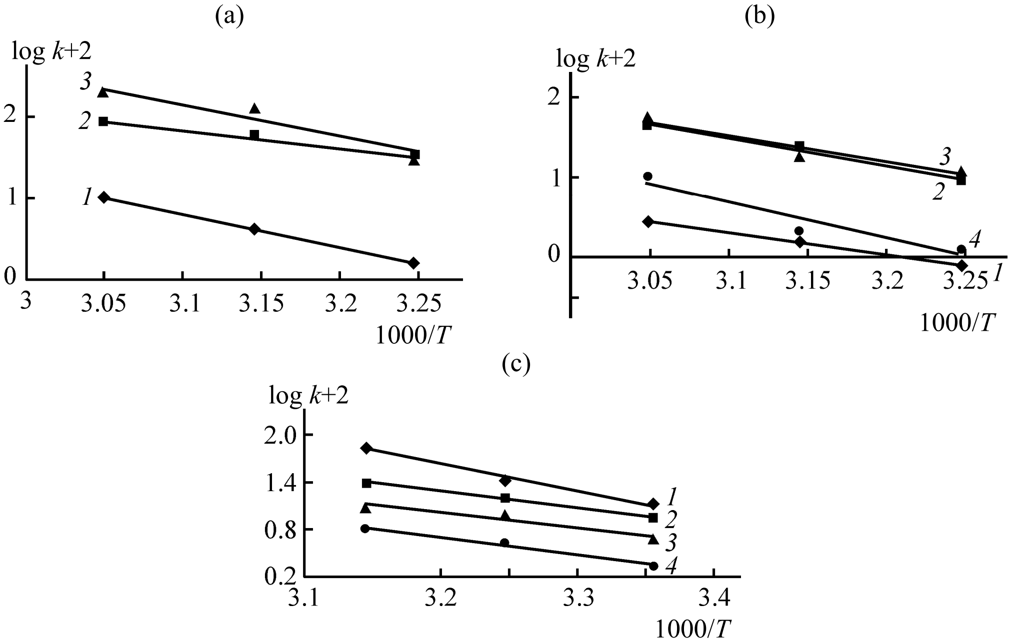


Fig. 5. Arrhenius plots for the hydrogen peroxide decomposition in the presence of complex **I** (a), **II** (b) and **III** (c). X = Cl (*1*), Br (*2*), I (*3*) and NCS (*4*).

relative to $[Cat]_0$ is more than one order of magnitude which makes quite probable the zero order in H_2O_2 when H_2O_2 excess is more than two orders of magnitude, for example, when $[H_2O_2]_0 = 4.2\times10^{-1}$ M. Thus, the $n_{H2O2} < 1$ observed in a number of cases is due, obviously, to an alternative route when the reaction rate is independent of $[H_2O_2]_0$: the catalyst is saturated with the substrate.

For the complexes **I–III** the found linear correlation $C = (1.6\pm0.1)n_{Cat} - (0.5\pm0.1)$ ($R^2 = 0.95$, $N = 10$, $s_y = 0.07$) (Fig. 4a) is quite close, with an exception of chloride ($n_{Cat} = 0.6$) and thiocyanate ($n_{Cat} = 0.5$) complexes **II**. Note that this trend (parallel changes of the compared values) is maintained qualitatively (Fig. 4b) also for the total reaction, while in the coordinates C–n_{H2O2} scatter of points is typically spread.

Original series of activity, depending on the nature of the acido-ligand in the considered complexes are evident (Fig. 5) also at the comparisons of the Arrhenius plots: **I** (Cl < Br ≤ I), **II** (Cl < NCS < Br ≈ I) and **III** (NCS < I < Br < Cl). In addition, in each reaction series for a pair of complexes a point of intersection appears (isokinetic temperature, T_{iso}) in the experimental temperature range [**I**(Br, I), T_{iso} = 298 K] or somewhat below it [**II** (Cl, NCS), T_{iso} = 299K; **III** (Cl, Br), T_{iso} = 290K]. In other words, in those cases where T_{iso} is close to room temperature (see also Table 1), the rate of reaction is insensitive to the nature

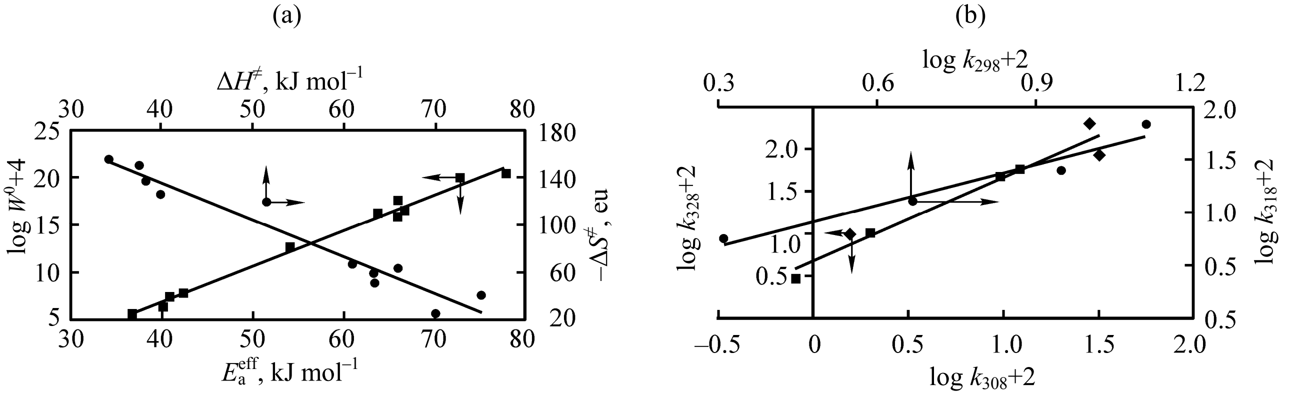


Fig. 6. Isokinetic relationships between the parameters of activation (a) and in the Exner coordinates (b) **I** (♦), **II** (■), **III** (●) for the hydrogen peroxide decomposition in the presence of complexes **I–III**.

of the acido-ligand X (isokinetic substituent [23]). Characteristically, in the remaining cases (Fig. 5) the Arrhenius plots have traditional view with the potential T_{iso} at temperatures higher than the experimental ones.

The discovered isokinetic relationship [23] between the parameters of activation (Fig. 6a) demonstrate the presence of a common compensation effect in the three reaction series (N = 11) $\Delta S^{\#} = (3.0\pm0.3)\Delta H^{\#} - (254\pm14)$ (R^2 = 0.94, s_y = 12).

However, given that the values of $\Delta H^{\#}$ and $\Delta S^{\#}$ contain large experimental error and depend on each other due to the way of their determination [23], we found (Fig. 6a), that in this case the isokinetic relations were reliably seen in the coordinates (log W^0 – E_a^{eff})[1]: log $W^0 = (0.36\pm0.01)E_a^{eff} - (7.3\pm0.7)$ (R^2 = 0,99; s_y = 0.6).

At the same time, in the Exner's coordinates (Fig. 6b) log k_{T2} – log k_{T1} ($T_2 > T_1$)[2] the isokinetic relations are detected as two straight lines, corresponding to complexes **I** and **II:** log k_{328} = (1.0±0.1) log k_{308} + (0.7±0.1); R^2 = 0.95; N = 7; s_y = 0.16, and to complexes **III**, log k_{318} = (1.3±0.2) log k_{298} + (0.3±0.2); R^2 = 0,94; N = 4; s_y = 0.14), which is obviously due not only to the difference in the temperature intervals, but also in the reaction mechanisms in each of the discussed reaction series.

Indeed, the attempt to approximate the whole array of points (Fig. 6b) by one straight line results in significantly poorer correlation: R^2 = 0.92; s_y = 0.17.

A similar comparison of the log k_T values for the interval 308–318 K leads to the equation log k_{318} = (1.0±0.1) log k_{308} + (0.2±0.1) (R^2 = 0.94; N = 11; s_y = 0.17), and while to the series of complexes **I** and **II** a similar equation corresponds, log k_{318} = (1.0±0.1) log k_{308} + (0.3±0.1) (R^2 = 0.96; N = 7; s_y = 0.17), the isokinetic relation for the complexes **III** is described by equation log k_{318} = (1.3±0.2) log k_{308} – (0.1±0.2) (R^2 = 0.95; N = 4; s_y = 0.12), almost like a similar equation (see above) for the range 298–318 K .

Summarizing the analysis of the detected isokinetic relations, we can reasonably assume that the mechanisms of decomposition of H_2O_2 in the presence of mononuclear complexes **I, II** and binuclear complexes **III** are similar, but not identical.

It is known [24] that in the hydrogen peroxide decomposition catalyzed by transition metal complexes (Haber-Weiss cycle) the key role plays the processes similar to the Fenton reaction:

$$M^{n+} + H_2O_2 \rightarrow M^{n+1} + HO^- + HO^{\cdot}.$$

It is possible that in our case the transition Co(II) → Co(III) is realized as a result of the transformation (via a cyclic transition state, *TS*) of the original complex (*St*) into the tetragonal intermediate (zwitterion Im^{II}, containing coordinated HOO^- anion), in which the endocyclic (chelate) tertiary nitrogen atom of the ligand L can promote deprotonation of H_2O_2 followed by homolytic cleavage of the O–O bond and the release of hydroxide anions, leading to intermediate Im^{III}.

Clearly, such a proton transfer from hydrogen peroxide (via a five-membered ring) on the spatially hindered tertiary nitrogen atom requires a certain strain of *TS*. We believe that Scheme 1 does not contradict the

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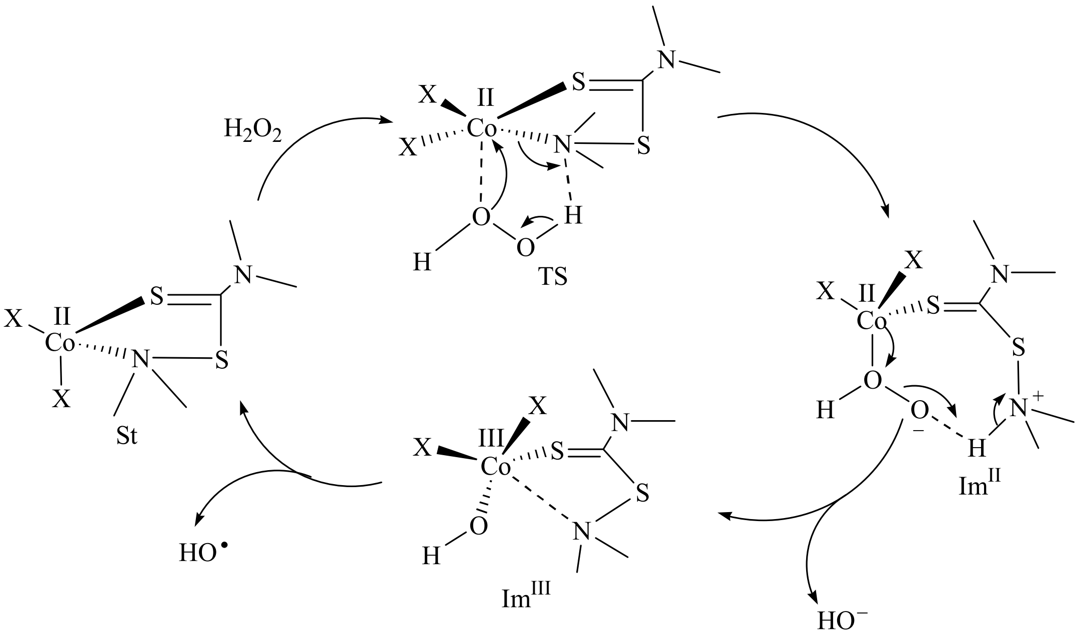
[1] See footnote (a) to Table. 1. Note also that there is a sufficiently close relationship $\Delta S^{\#} = (8,4\pm0,5)$ log $W^0 - (201\pm8)$ (R^2 = 0.96; s_y = 9.6).

[2] A greater difference between T_1 and T_2 is desirable [23].

Scheme 1.



change in the kinetic and activation parameters of the reaction (Table 1) depending on the structure and composition of the chelating ligand L and the nature of acido-ligands **X** in complexes **I–III**, and the results of our previous work [11].

Following the above, we have attempted to estimate with Edwards' equation [25] the effect of the nature of acido-ligands **X** (Table 2) on the catalase activity of complexes **I–III.** The ligand X determines the electron density of the metal center as well as the "promotion" of the H-bonds Co–X···H–O– (see Schemes 2 and 3) formation .

Unfortunately, for complex **II** we do not find a correlation between the quantities of log k_{308} and constants En and H, as well as a linear combination of the two latter. For log k_{318} and log k_{328} of these complexes the one- and two-parametric linear correlations are insufficient, $R^2 \leq 0.72$.

Similar pattern is noted for log k_{308} in the presence of halide complexes **I**, however the correlation of log k_{318} and log k_{328} with the basicity (H) of halide anions (conjugate bases) X^- for these complexes is acceptable (Table 2), while there is no correlation with En constants.

The pattern is different for complexes **III**: the values of log k_T are approximated acceptable by Edwards' equation ($\alpha < 0$, $\beta > 0$), therewith the sensitivity of the reaction rate to the polarizability (En) of

Table 2. Parameters of Edwards equation $\log k = \log k_0 + \alpha\text{En} + \beta\text{H}$ for the hydrogen peroxide decomposition in the presence of complexes **I** and **III**[a]

Comp. no.	T, K	$-\alpha$	β	N	$\log k_0+2$	R^2	s_y
I	308	Insignificant	–(0.2±0.1)	3	–0.2±0.8	0.72	0.6
	318	The same	–(0.24±0.08)	3	0.03±0.5	0.91	0.3
	328	″	–(0.21±0.05)	3	0.5±0.3	0.94	0.2
III	298	0.9±0.3	0.05±0.02	4	2.4±0.5	0.92	0.2
	308	0.8±0.2	0.05±0.02	4	2.6±0.4	0.96	0.12
	318	1.2±0.1	0.06±0.01	4	3.5±0.1	0.99	0.04

[a] En = (E^0 + 2.6) is the oxidation potential (polarizability) of the ligand X, H = (pK + 1.74) is the basicity of the conjugate acid HX [22].

Table 3. Parameters of the Edwards equation log W^0 = log W + αEn + βH for the hydrogen peroxide decomposition in the presence of complexes **I, II**, and **III**

Comp. no.	T, K	–α	–β	N	log W^0+4	R^2	s_y
I	328	0.6±0.2	0.13±0.01	4	0.7±0.3	0.99	0.1
II	318	0.6±0.5	0.07±0.04	4	0.9±0.9	0.83	0.3
III	298	0.44±0.05	0.017±0.004	4	0.6±0.1	0.99	0.03
	308	0.44±0.05	0.021±0.004	4	0.9±0.1	0.99	0.05
	318	0.8±0.1	0.00±0.01	4	1.8±0.2	0.98	0.08

ligands **X** exceeds markedly that to the basicity (|α| >> |β|). Note also that in the case of complexes **I** and **III** (Table 2) the increase in temperature increases significantly the strength of relations (R^2) between the values of log k_T and the Edwards' constants.

In terms of the above relationship between the values of log k and log W^0, and taking into account the smaller error in the calculation of the latter, we found it interesting to consider the relation between the quantities of log W^0 and Edwards' constants. As shows Table 3, such relations are detected and can be qualitatively assessed (in accordance with the Chaddok scale [26]) as high (for complex **II**) and very high (for the complexes **I** and **III**). Notably, however, that in the case of complexes **II** the R^2 values for the discussed equations log $W^0{}_{308}$ and log $W^0{}_{328}$ and are only 0.71 and 0.56, respectively. Also note a marked similarity between the parameters of the Edwards equation for log W^0_{328} of complexes **I** and log W^0_{318} of complex **II**. In addition, common to all three reaction series in this case is the dominance of the polarizability factor of acido-ligands X^- over their basicity (|α| >> |β|), which in the case of log k (Table 2) is observed only for complexes **III**.

According to the discussed parameters (Table 3), the influence of the ligand **X** basicity on the rate of hydrogen peroxide decomposition in the presence of complexes **III** at 318 K is leveled: β = 0. However, attempts to approximate the values of log W^0_{298} and log W^0_{318} of these complexes by a one-parameter equation (without the constant H), leads to correlation with the coefficients of determination 0.86 and 0.80, respectively.

Comparing the structural formulas (molecular graphs) of the complexes **I–III** one can see that the complex **II** is largely similar to the complex **I** and differs from complex **III** by the presence of a second metallocycle associated with the first through the piperazine bridge. If, as a first approximation, we neglect the influence of the various gem-dimethyl and gem-diethyl groups at the tertiary nitrogen atoms of the chelates, as well as the difference in the substituents at the exocyclic nitrogen atoms, it can be assumed that the electron density on the cobalt atoms of the complexes **I–III** at the constant acido-ligands **X** is approximately the same. Then we can expect that at the same concentration of the corresponding complexes **I–III** in the reaction mixture, the rate of hydrogen peroxide decomposition in the presence of complexes **I** and **II** will be close ($W^0_{\mathbf{II}}/W^0_{\mathbf{I}} \approx 1$). In the case of binuclear complex **III**, in similar conditions, when the effective concentration of Co(II) is twice that in the presence of mononuclear complexes **I** and **II**, the reaction rate should be close to that of complex **II** ($W^0_{\mathbf{II}}/W^0_{\mathbf{III}} \approx 1$), if activation of H_2O_2 occurs at a metal center[3] (see above). If the activation of H_2O_2, similarly [27], occurs on the bimetallic center, one would expect an easier cleavage of the O–O bonds, that is, greater acceleration and, therefore, $W^0_{\mathbf{II}}/W^0_{\mathbf{III}} < W^0_{\mathbf{II}}/W^0_{\mathbf{I}}$. As can be seen from Fig. 7, comparison in pairs the values of $W^0_{\mathbf{II}}$ (chosen as the "standard" series) with $W^0_{\mathbf{I}}$, and $W^0_{\mathbf{III}}$ leads to a linear relationship, the regression coefficients are significantly distinguishable and qualitatively as expected:

$$W_{\mathbf{II}} = (0.7\pm0.1)W_{\mathbf{I}} + (1.3\pm0.4);\ R^2 = 0{,}95;\ n = 5;\ s_y = 0.7,$$

$$W_{\mathbf{II}} = (0.4\pm0.1)W_{\mathbf{III}} - (0.2\pm0.2);\ R^2 = 0{,}94;\ n = 6;\ s_y = 0.2.$$

Thus, we can reasonably assume that in the case of binuclear complex **III** the two-point activation of H_2O_2 requiring, for obvious reasons, the preliminary conversion of *chair* conformation of the piperazine fragment to the *boat*-like *twist* form:

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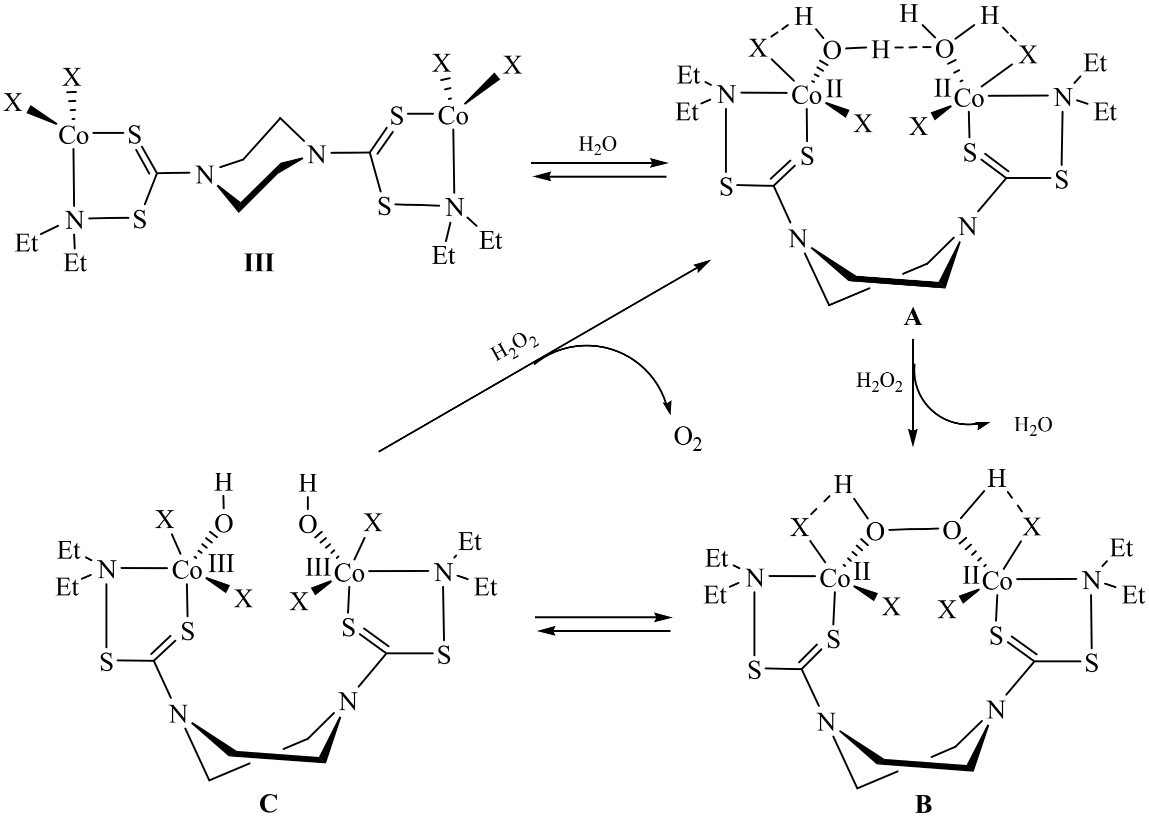
[3] We exclude the simultaneous (synchronous) activation of two molecules of H_2O_2 in each of the metal centers of dinuclear complexes **III**, as in this case $n_{H2O2} \rightarrow 2$, which is inconsistent with experiment (Table 1).

Scheme 2.



According to [28], the the *chair* conformer of piperazine is more stable than *boat* by 16 kJ mol^{-1}, and the barrier for the conversion of *N*,*N*'-dimethylpiperazine is (56±2) kJ mol^{-1}, which is 20–30 kJ mol^{-1} lower than the free energy of activation of the reactions in the presence of complexes **I**–**III** (Table 1). In addition, the intermediate **A** (Scheme 2) can be probably stabilized by hydrogen bonds of coordinated water molecules both among themselves and with the acido-ligands **X**. The subsequent catalytic cycle **A**–**B**–**C**–**A** shown in Scheme 2 corresponds to that proposed in [27] for the decomposition of H_2O_2 in the presence of binuclear complex $[Mn_2(NAPH)(\mu\text{-}OAc)(phen)_2]\cdot OAc$, where NAPH is 1,8-naphthalate dianion and phen is phenanthroline.

It can also be seen from Fig. 7 that the points corresponding to the complex **I**(Br) "gravitate" to the "family" of complexes **III**, and the points of the complex **III**(I) "gravitate" to the "family" of complexes **I**. It is possible that the latter is due to the difficulty of assembly of the intermediate **A** (Scheme 2) because of the larger (in comparison with the rest of acido-ligands **X**) iodide anion and its higher "softness" which will reduce the strength of H-bonds Co–I···H–OH. These factors make it possible to assume that in the case of binuclear complex **III**(I) there is a single-site activation of hydrogen peroxide, such as those shown in Scheme 1, that is, second metal center of the complex **III**(I) is excluded from the activation of H_2O_2.

As for the complex **I**(Br), its preliminary dimerization (as limiting step) to form 10-membered macro

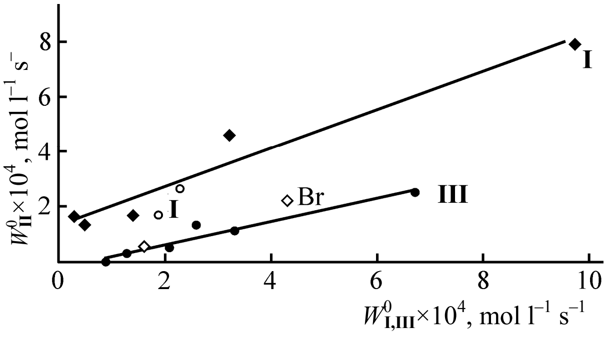
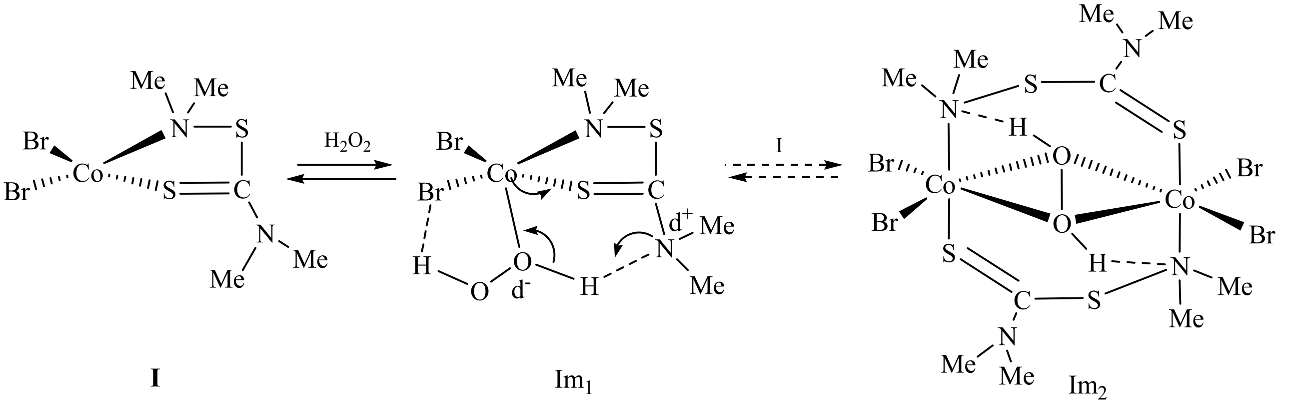


Fig. 7. Comparison of the rates of hydrogen peroxide decomposition in the presence of complex **II** with the corresponding rates in the presence of complex **I** (♦,◊) and **III** (●,○). See explanation in the text.

Scheme 3.



chelate (Im_2, Scheme 3) is excluded, as in the presence of this complex the value $n_{Cat} = 1$ (Table 1). Then the possibility of double-site activation of hydrogen peroxide in this case can be explained (with great caution) assuming that the rate-limiting step of the process is the formation of complex **I**·H_2O_2 (Im_1, Scheme 3).

The proton transfer from the coordinated H_2O_2 molecule on dimethylamino group (like the one shown in Scheme 1) should facilitate the opening of metallocycle under the influence of a second molecule of the complex **I**(Br) and the formation of the macrocyclic intermediate Im_2, containing coordinated H_2O_2 molecule in the cavity, similar to intermediate **B** (Scheme 2), which may be one of the stages of the corresponding catalytic cycle. To some extent, in favor of this assumption is the maximum negative value of the activation entropy (Table 1) of the complex **I**(Br) in comparison with chloride and iodide complexes.

Note also that adding points of the complex **III**(I) (Fig. 7) to the "family" of complexes **I**, and those of complex **I**(Br) to the "family" of complexes **III** does not change the discussed dependences, but in the latter case the quality of the relevant correlations is noticeably deteriorated: $R^2 = 0.93$, $n = 7$, $s_y = 0.7$ for $W_{\mathrm{II}}/W_{\mathrm{I}}$ and $R^2 = 0.90$, $n = 8$, $s_y = 0.3$ for $W_{\mathrm{II}}/W_{\mathrm{III}}$.

Summarizing the research, it may be noted that the catalase activity of the studied cobalt(II) complexes is determined by both composition and structure of chelating *N,N,N',N'*-tetrasubstituted thiocarbamoylsulfenamide and the nature of the acido-ligands. The only exceptions are thiocyanates, which are the least active among the complexes **I–III**. The nature of series of activity of the corresponding complexes **I–III** differ appreciably, which affects the enthalpy and entropy contributions to the free activation energy (Table 1) that in each reaction series does not vary by more than 10 kJ mol^{-1}.

In the studied conditions, the kinetics of the H_2O_2 decomposition in the presence of complexes **I–III** is quite complicated: fractional (n <1) values of the partial orders of the reaction (Table 1) with respect to the catalyst and H_2O_2 indicate that (as in [22]) in addition to the Haber-Weiss catalytic mechanism ($Co^{2+} + H_2O_2 \rightarrow Co^{3+}OH + HO^\bullet$) also an alternative non-catalytic (radical) route: $HO^\bullet + H_2O_2 \rightarrow H_2O + HOO^\bullet$ can contribute. The complexity of the hydrogen peroxide activation by the complexes **I–III** is confirmed by the presence of several points of intersection (T_{iso}) in the Arrhenius plots (Fig. 5), in the experimental temperature range or slightly below it [23].

The observed isokinetic relationships between rate constants and activation parameters, as well as the comparison of the $W^0_{\mathrm{II}}/W^0_{\mathrm{III}}$ and $W^0_{\mathrm{II}}/W^0_{\mathrm{I}}$ relationships allow us to assume reasonably that the mechanism of H_2O_2 decomposition in the presence of mononuclear complexes **I, II** and binuclear complexes **III** are of similar, but not identical, character. That is, the majority of the complexes **I, II** most likely perform single-site activation of H_2O_2 while complexes **III** acts as double-site activators.

We believe that the variation in the structure of thiocarbamoylsulfenamide and nature of acido-ligands will bring greater clarity in understanding the mechanisms of catalase activity of the complexes similar to those considered in this paper.

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