COBALT COMPLEXES—HYDROPHOBIC DERIVATIVES OF VITAMIN B_{12} IN CATALYSIS AND ELECTROCATALYSIS

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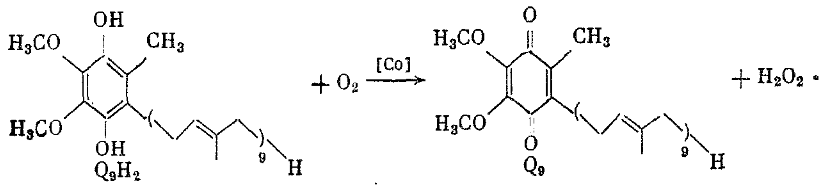
Studies have recently been successfully developed on modeling of enzymatic catalysis with organic transition metal complexes [1]. Catalytic activity which models the function of the ubiquinone oxidase segment of biological electron-transport chains of respiration and photosynthesis is observed in homogeneous reactions for a large group of cobalt and copper complexes [2]. These complexes also exhibited catalytic activity in the reaction of cathode reduction of O_2 in soft conditions [3]. The cobalt(II) decamethyloctadehydrocorrin complex related to vitamin B_{12} is the most active in the reactions studied. In this respect, it was interesting to study the catalytic activity of Co^{II} and Co^{III}—hydrophobic vitamin B_{12} derivatives—cobryinic acid alkyl ester complexes, whose structure is shown below.

The catalytic activity of the synthesized complexes in the homogeneous reaction of oxidation of quinoid substrates by dioxygen was compared with the electrocatalytic activity in the reaction of cathode reduction of dioxygen in adsorption of the complexes on the surface of an electrode with different hydrophoby in the present study.

RESULTS AND DISCUSSION

The catalytic activity of the cobalt corrin complexes was studied in the reaction of oxidation of two quinoid substrates by molecular oxygen: polar hydroquinone and hydrophobic quinol Q_9H_2, an analog of natural coenzyme Q_{10}, the key component in electron-transport chains in the living cell



It was found that the complexes studied on the whole exhibit marked catalytic activity which exceeds the activity of the starting $B_{12}OH$. The data obtained are reported in Table 1. Oxidation of quinols takes place with the formation of H_2O_2, which was recorded with a benzidine probe [4]. It was found that the reaction is of the first order with respect to the substrate (hydroquinone or Q_9H_2) and zero order with respect to O_2, and the rate can be expressed by the following equation: $v = k[QH_2][Co]$.

The experiments in the absence of O_2 confirmed that Co^{III} complexes are reduced by ubiquinol Q_9H_2. This process is probably the first stage of the catalytic reaction. It should be noted that complexes with one or two CN groups stably bound with cobalt as the axial ligands do not exhibit catalytic activity in oxidation. The presence of two free coordination sites is apparently necessary for the manifestation of catalysis. The set of these data suggest that the mechanism of the reaction consists of coordination of the oxidized substrate and oxygen with respect to axial positions 5 and 6 of the cobalt complex with the intermediate formation of a ternary complex [5]. The following scheme of the reaction, in agreement with the kinetic data, can thus be hypothesized

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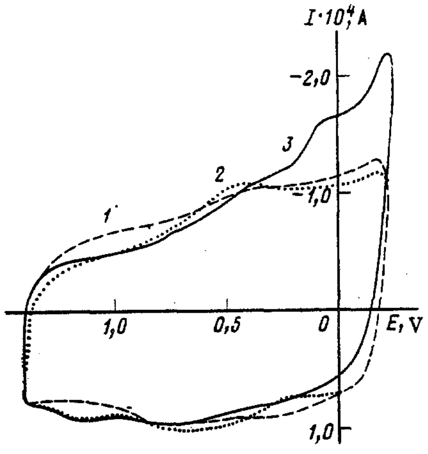

Fig. 1

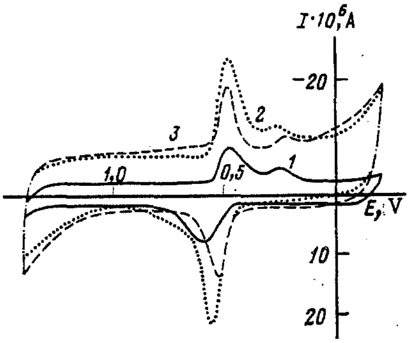

Fig. 2

Fig. 1. I, E curves obtained on: 1) pyrographite electrode; 2) pyrographite electrode with adsorbed complex (I), first pulse; 3) cyclic curve.

Fig. 2. I, E curves measured on a carbon black electrode modified with Q_9 (1), Q_9 and complex (VI) (2), Q_9 and complex (VIII) (3). Phosphate–alkali buffer solution, pH 7.5; ν = 0.002 V/sec.

$$[\mathrm{Co^{III}}]^{2+} + \mathrm{QH_2} \xrightarrow{\text{slow}} [\mathrm{Co^{II}}]^{+}\cdot\dot{\mathrm{Q}}\mathrm{H} + \mathrm{H^+}$$

$$[\mathrm{Co^{II}}]^{+}\cdot\dot{\mathrm{Q}}\mathrm{H} + \mathrm{O_2} \rightarrow [\mathrm{Co^{II}}]\cdot\dot{\mathrm{Q}}\mathrm{H}\cdot\mathrm{O_2}$$

$$[\mathrm{Co^{II}}]\cdot\dot{\mathrm{Q}}\mathrm{H}\cdot\mathrm{O_2} + \mathrm{H^+} \rightarrow [\mathrm{Co^{III}}]^{2+} + \mathrm{Q} + \mathrm{H_2O_2}$$

The dependence of the catalytic activity on the hydrophoby of the complexes in oxidation of fat- and water-soluble substrates was very interesting. As Table 1 shows, in oxidation of a hydrophobic substrate (quinol Q_9H_2), hydrophobic complexes: cobryinic acid heptyl esters, both in the series of uncharged complexes of $\mathrm{Co^{III}}$ (III) and in the series of cationic complexes of $\mathrm{Co^{II}}$ (VIII), exhibited the highest catalytic activity. The activity of the complexes decreases with a decrease in the length of the carbon chain in the corresponding ester: (III) > (II) > (I); (VIII) > (VII) > (VI).

The most hydrophilic complexes, dihydroxycobryinic acid (IX) and dihydroxycobinamide (X), did not exhibit any catalytic activity in general in oxidation of hydrophobic ubiquinol Q_9H_2. At the same time, the high rate of oxidation of Q_9H_2 by hydrophobic complexes can be attributed to the presence of affinity between them due to hydrophobic reactions. It is very indicative that in oxidation of a hydrophilic substrate (hydroquinone), the order of activity of the complexes is reversed, i.e., the rate of oxidation by heptyl cobryinates (III) and (VIII) is lowest in the corresponding series (Table 1).

The CoK_{β_5} x-ray spectra of vitamin $\mathrm{B_{12}CN}$, $[\mathrm{Co^{III}(OH)(CN)}]_{\mathrm{Me}}$ and $[\mathrm{Co^{III}(OH)(CN)}]_{\mathrm{Hp}}$ were obtained to determine the features of the electron structure of the cobalt corrin complexes and their effect on the catalytic activity. It was found that the position of the maximum of the CoK_{β_5} spectrum of these complexes is the same. This indicates that the charged states of Co within the boundaries of the first coordination sphere remain unchanged. The energies of the 1s levels of nitrogen (ESCA data) also remain constant, which indicates the invariability of the charged state of the nitrogen atoms in their first coordination sphere. On the whole, the data obtained indicate that the electron density in the region of the coordinating atoms of $\mathrm{Co^{III}}$ corrin complexes is the same.

Since the electron effect of ester substituents (within the limits of sensitivity of the method) is not transmitted to the nitrogen and cobalt atoms, it is possible to conclude that the observed differences in the rate of the oxidation reaction for the corrin complexes are due to the contribution of hydrophobic reactions to the total energy of the reaction of the quinoid substrate and catalyst. Confirmation of the contribution of hydrophobic reactions in the catalysis of oxidation of quinoid substrates by the complexes was also obtained in electrochemical experiments in which the half-reaction of the catalytic cycle: reduction of

TABLE 1. Catalytic Activity of the Complexes [v^0, 10^7 moles/(liter·min)] in the Reaction of Oxidation of Quinoid Substrates by the Oxygen in the Air (concentration of substrates 10^{-4} mole/liter, concentration of complexes 10^{-6} mole/liter for Q^9 and 10^{-5} mole/liter for hydroquinone)

Complex	Q_9	Hydroquinone	Complex	Q_9	Hydroquinone
$[Co^{III}(OH)_2]_{Me}$ (I)	2,6	8,0	$[Co^{II}]_{Bu}(ClO_4)$ (VII)	2,3	7,3
$[Co^{III}(OH)_2]_{Bu}$ (II)	4,3	6,3	$[Co^{II}]_{Hp}(ClO_4)$ (VIII)	2,8	6,0
$[Co^{III}(OH)_2]_{Hp}$ (III)	5,6	5,3	$[Co^{III}(OH)_2]_H$ (IX)	0	8,3
$[Co^{III}(OH)(CN)]_{Me}$ (IV)	0	0	$[Co^{III}(OH)_2]_{NH_2}$ (X)	0	8,7
$[Co^{III}(CN)_2]_{Me}$ (V)	0	0	$B_{12}OH$ (XI)	0,4	0,7
$[Co^{II}]_{Me}(ClO_4)$ (VI)	1,3	8,0			

molecular oxygen, was modeled. In these experiments, the electron donor (quinol) is substituted on the electrode on which the complex is applied. Pyrographite, whose surface contains fragments of quinoid structures [6], was selected as the electrode support. It was found that the complexes are unstably adsorbed on the surface of the pyrographite, indicated by the possibility of their removal when the electrode is washed with alcohol. Adsorption of the complexes results in a decrease in the polarization capacity of the electrode (Fig. 1). The observed decrease in the capacity is apparently due to displacement of water molecules from the double layer. The shape of the volt–ampere curves measured in the 1.4 to –0.2 V potential range on the electrode with the adsorbed complex is not a function of the type of complex.

It was found that the complexes adsorbed on the pyrographite electrode exhibit catalytic activity in electrolytic reduction of O_2. Complex (I), whose presence on the surface of the electrode causes a 0.170-V shift of the polarization curve to the positive side (Table 2), exhibits the highest activity, evaluated by the shift of the polarization curve relative to the background with a constant current (ΔE). The order of the activity of the complexes in the reaction of electrolytic reduction of oxygen of (I) > (II) > (III) coincides with the order of the activity of the complexes in the homogeneous reaction of oxidation of hydroquinone and is the reverse of the order of the activity in catalysis of oxidation of Q_9H_2 by molecular oxygen. It is possible to hypothesize that the affinity of the catalyst for the hydrophilic surface of the pyrocarbon decreases with an increase in its hydrophoby. As a consequence, the amount of adsorbed catalyst is smaller and the activity of the electrode in the reaction of electrolytic reduction of molecular oxygen is lower. The fact that the polarization capacity of the electrodes with the adsorbed catalyst decreases more the more hydrophilic the complex is confirms this hypothesis.

We attempted to increase the affinity of the complex for the surface of the electrode by altering its hydrophoby. Carbon black modified with Q_9 was used as the electrode material for this purpose. Two cathode maxima (0.46 and 0.25 V) and an anode maximum (0.6 V) are observed in the dynamic potential curves of this electrode (Fig. 2), characteristic of the quinone–hydroquinone transition [6]. Adsorption of the complexes on the surface of the carbon black electrode modified by Q_9 does not result in the appearance of new maxima on the dynamic potential curves (Fig. 2). The presence of the complexes is manifested by an increase in the amount of electricity consumed in redox transformations of Q_9 (from $4.1 \cdot 10^{-3}$ C in the absence of the complex to $1.4 \cdot 10^{-2}$ C in its presence), and by a change in the ratio of the value of the currents of the cathode maxima and an increase in the degree of reversibility of the redox transformations of the complexes, determined with the difference ($\Delta E'$) in the position of the anode and cathode maxima (Table 2). The reversibility of the maxima increases with an increase in the hydrophoby for both cationic (VI)-(VIII) and uncharged (I)-(III) complexes. The increase in the reversibility of the I, E curves, which is correlated with an increase in the hydrophoby of the complexes, indicates acceleration of the redox process with potentiation of hydrophobic reactions in the quinone–corrin system. In studying the catalytic activity of these electrodes in the reaction of electrolytic reduction of oxygen, it was shown that the observed features significantly differ from charged and uncharged complexes With an increase in the length of the side chain of the uncharged complexes, the catalytic activity virtually does not change, while it increases with an increase in the hydrophoby (Table 2) to the level of the activity of the uncharged complexes in a number of cationic complexes. This is apparently due to the fact that the uncharged complexes on the whole have

TABLE 2. Electrocatalytic Activity of the Complexes in the Reaction of Cathode Reduction of Molecular Oxygen and Degree of Reversibility of Redox Transformations of the Complexes

Complex	Pyrographite	Carbon black modified with Q_9	$\Delta E'$, V	Complex	Pyrographite	Carbon black modified with Q_9	$\Delta E'$, V
	ΔE, V				ΔE, V		
	$I=2{,}25\cdot10^{-5}$, A	$I=15{,}0\cdot10^{-5}$, A			$I=2{,}25\cdot10^{-5}$, A	$I=15{,}0\cdot10^{-5}$, A	
(I)	0,170	0,100	0,050	(VI)	–	0,020	0,045
(II)	0.110	0,095	0,035	(VII)	–	0,060	0,030
(III)	0,035	0,100	0,030	(VIII)	–	0,095	0,010

a high affinity for the hydrophobic electrode, while the cationic complexes exhibit a lower affinity for it, and against this background, the increase in the hydrophoby has a greater effect due to lengthening of the side chains.

It was thus shown that the stage of the reaction of the catalyst with the electron donor is very important for both homogeneous catalytic oxidation of quinols by molecular oxygen and for electrolytic reduction of molecular oxygen. The efficiency of this reaction is determined by the correspondence of the hydrophobic properties of the catalyst and substrate.

EXPERIMENTAL

Cobryinic acid heptamethyl ester $[Co^{III}(CH)_2]_{Me}$ was synthesized according to [7] with vitamin $B_{12}OH$ obtained from the Kurgan Synthesis Combine.

Heptabutyldihydroxycobryinate $[Co^{III}(OH)_2]_{Bu}$ and heptaheptyldihydroxycobryinate $[Co^{III}\cdot(OH)_2]_{Hp}$ were prepared from $[Co^{III}(OH)_2]_{Me}$ (50 mg) by boiling for 3 h in 100 ml of a mixture of H_2SO_4 with n-butyl or n-heptyl alcohol (1:20 by volume) in an Ar current. Then 150 ml of chloroform was added to the cooled reaction mixture and it was washed with ice water until the acid reaction disappeared. The extract was dried over anhydrous Na_2SO_4 and vacuum evaporated at 40°C. All of the Co^{III} complexes were purified by column chromatography on silica gel 5/40. Elution was conducted with the hexane–chloroform–methanol–n-butanol mixture (10:3:1:0.2). The yield of $[Co^{III}(OH)_2]_{Bu}$ and $[Co^{III}(OH)_2]_{Hp}$ was ~85%; UV spectrum (λ_{max}, nm (ε), CH_2Cl_2): 262, ($2.54\cdot10^4$), 344 ($1.04\cdot10^4$), 374 ($1.03\cdot10^4$), 580 ($0.76\cdot10^4$). IR spectrum (KBr, ν, cm^{-1}): 1740 (C=O).

Heptamethyldihydroxycobryinate $[Co^{III}(OH)_2]_{Me}$: R_f 0.45 on Silufol in the hexane–chloroform–methanol–n-butanol system (5:4:1:0.2). Found: C 57.69, H 6.95, N 5.65%. $C_{52}H_{74}Co_1N_4O_{16}$. Calculated: C 58.37, H 6.92, N 5.24%. Mass spectrum: 1036 (100%) M^+ 2 OH.

Heptabutyldihydroxycobryinate $[Co^{III}(OH)_2]_{Bu}$: R_f 0.65 in the same conditions. Found: C 63.98, H 8.38, N 4.49%. $C_{73}H_{116}Co_1N_4O_{16}$. Calculated: C 64.27, H 8.51, N 4.11%.

Heptaheptyldihydroxycobryinate $[Co^{III}(OH)_2]_{Hp}$: R_f 0.60 in the same conditions. Found: C 67.97, H 9.51, N 3.56%. $C_{94}H_{158}Co_1N_4O_{16}$. Calculated: C 68.07, H 9.54; N 3.38%.

Heptaalkylcobryinate perchlorates $[Co^{II}]_{Alk}(ClO_4)$ were prepared by the method in [8] using the corresponding heptaalkylcobryinates. They were purified by three precipitations from benzene solution with dodecane.

Heptabutylcobryinate perchlorate $[Co^{II}]_{Bu}(ClO_4)$. Found: C 61.15, H 7.85, N 4.21%. $C_{73}H_{114}Cl_1Co_1N_4O_{18}$. Calculated: C 61.32, H 7.98, N 3.92%.

Heptaheptylcobyrinate perchlorate $[Co^{II}]_{Hp}(ClO_4)$. Found C 65.38, H 9.05, N 3.45%. $C_{94}H_{156}Cl_1Co_1N_4O_{18}$. Calculated: C 65.49, H 9.06, N 3.25%.

The spectral characteristics of the perchlorates are similar to those described in [8].

Heptaalkyldicyanocobryinates $[Co^{III}(CN)_2]_{Alk}$ were prepared from the corresponding dihydroxycobryinates dissolved in chloroform with a 10% aqueous solution of KCN. The chloroform solution was dried with anhydrous Na_2SO_4 and vacuum evaporated without further purification. Yield of 95%. The spectral characteristics are similar to those described in [9].

Heptaalkylcyanohydroxycobryinates $[Co^{III}(OH)(CN)]_{Alk}$ were prepared from the corresponding dicyanocobryinates dissolved in chloroform with a 40% aqueous solution of HCl. The chloroform solution was dried with anhydrous Na_2SO_4 and vacuum evaporated without further purification. Yield of 90%. UV spectrum (λ_{max}, nm (ε)): 370 ($1.92 \cdot 10^4$), 535 ($0.84 \cdot 10^4$), 570 ($0.84 \cdot 10^4$). IR spectrum (KBr, ν, cm^{-1}): 1760 (C=O), 2160 (C≡N) cm^{-1}.

Dihydroxycobinamide $[Co^{III}(OH)_2]_{NH_2}$ was prepared according to [10].

Dihydroxycobryinic acid $[Co^{III}(OH)_2]_{Hp}$ was prepared from $[Co^{III}(CH)_2]_{Me}$ (50 mg) by boiling for 10 min in 30 ml of a CH_3COOH–HCl mixture (3:1 by volume). It was salted out by conversion to the phenol complex with its subsequent decomposition with i-PrOH–Ccl_4 mixture (3:2). Yield of 80%.

The ubiquinone Q_9 was kindly provided by E. A. Obol'nikova (Vitamin Scientific and Industrial Association), and the hydroquinone was purified by two recrystallizations from acetone. The initial rate of oxidation of the substrates was used as the measure of the catalytic activity of the complexes.

The catalytic activity of the complexes in the reaction of ubiquinone Q_9H_2 by molecular oxygen was determined spectrophotometrically based on the increase in the optical density corresponding to the formation of quinone (λ 275 nm, ε 12,220 liters·$mole^{-1} \cdot cm^{-1}$) in isooctane–ethanol mixture, 1:1. Reduction of Q_9 to Q_9H_2 was conducted with $NaBH_4$ immediately before the experiment. The concentrations of ubiquinol and the complex were 10^{-4} and 10^{-6} mole/liter respectively.

The catalytic activity of the complexes in oxidation of hydroquinone was determined based on the decrease in the optical density corresponding to a decrease in the reduced form (λ 290 nm, ε 3000 liters·$mole^{-1} \cdot cm^{-1}$) in methanol. The initial concentrations of the hydroquinone and the complex were 10^{-4} and 10^{-5} mole/liter. The reactions were conducted at ~20°C in air.

The pyrographite electrode (new for each experiment) was a 5 × 10 mm plate. The pyrographite electrode was boiled for 15 min in an alkali and then repeatedly in twice-distilled product. Before each experiment, the electrodes were activated by cathode–anode polarization in the –0.2 – +1.4 V potential range. The complex was applied to the surface of the electrode from a solution in alcohol (10^{-5} mole/liter) and dried at ~20°C. The amount of the complex on the surface was 10^{-10} mole. When Pm-100 carbon black was used as the electrode material, a floating gas-diffusion electrode [11] was used. Q_9 was adsorbed on the carbon black from alcohol solution (10^{-3} mole/liter) for 2 h. The amount of Q_9 adsorbed on the surface was determined with the residual concentration of the mother solution on a Specord UV-VIS spectrophotometer. Q_9 was irreversibly sorbed in the amount of $4 \cdot 10^{-10}$ mole/mg of carbon black. The carbon black modified with Q_9 was pressed on the surface of the gas-diffusion electrode. The complex studied was applied to the electrode from alcohol solution (10^{-3} mole/liter) in the amount of $4 \cdot 10^{-10}$ mole/liter of carbon black.

The electrochemical measurements were conducted by the method of dynamic potential triangular pulses [12] in alkaline phosphate buffer solution ($\mu = 0.15$, pH 7.5). The buffer solution was prepared from twice-distilled water, especially pure NaOH, and recrystallized KH_2PO_4. All of the potentials are reported relative to a hydrogen electrode in the same solution. The capacitance of the electrodes was calculated in the 1.5-1.090 V potential region. The values of the amount of electricity was determined under the I, E curve in the potential region of +1.4 to –0.2 V.

The mass spectrum of $[Co^{III}(OH)_2]_{Me}$ was made by A. G. Zhukovskii and G. D. Tantsyrev (Institute of Chemical Physics, Academy of Sciences of the USSR) on a MI-1201 É mass spectrometer with ionization by fast atoms. A 10% solution of the substance in glycerin was used as the target, and bombardment was with Ar atoms with an energy of 5 kV.

The x-ray electron spectra were made by A. T. Kozakov, A. V. Nikol'skii, and A. T. Shuvaev on a spectrometer created at the Scientific-Research Institute of Physics at Rostov State University. Operating conditions: 9 kV, 60 mA, $5 \cdot 10^{-7}$·mm Hg vacuum. The samples were prepared by application to adhesive tape.

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CONCLUSIONS

The state of the reaction of the catalyst with the electron donor is important for both homogeneous catalytic oxidation of quinols by cobalt corrin complexes and for electrolytic reduction of oxygen on electrodes modified by these complexes; the efficiency of this reaction is determined by the correspondence of the hydrophobic properties of the catalyst and substrate.

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KINETICS OF OVERALL DECOMPOSITION OF OZONIDES OF 2,2'-METHYLENE-BIS-4-METHYL-6-TERT-BUTYLPHENYL ESTERS OF PHOSPHOROUS ACID

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A high oxidizing activity makes it possible to carry out various reactions with the participation of phosphite ozonides $(RO)_3P\cdot O_3$ [1, 3], especially as a result of their ability to decompose with the liberation of a singlet oxygen on heating or by the action of catalysts [4, 5]. In turn, a singlet oxygen ensures the occurrence of many chemical oxidation reactions [6]. The search for and study of new adducts of O_3 with phosphites is therefore very important. It is also interesting to study the factor determining the stability of $(RO)_3P\cdot O_3$, since to successfully use the phosphite ozonides in oxidative transformations, we must know their thermal stability.

In the present work, the results are reported of a study of the thermal stability of a series of ozonides of 2,2'-methylene-bis-4-methyl-6-tert-butylphenyl esters of phosphorous acid of different structure, and the influence of the nature of solvent on the rate of decomposition of $(RO)_3P\cdot O_3$ is revealed.

EXPERIMENTAL

Methyl-, ethyl-, phenyl-, α-naphthyl(2,2'-methylene-bis-4-methyl-6-tert-butylphenyl) phosphites (I)-(IV) were synthesized and purified according to [7]. Solvents CH_2Cl_2, $CHCl_3$, CCl_4, 1,2-$C_2H_4Cl_2$, CH_3CN, CH_3NO_2, Et_2O, i-C_3H_7OH, n-C_6H_{14}, i-$C_3H_7C_6H_5$, and C_6H_5Cl were thoroughly dried and purified according to [8, 9].

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