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Kinetic Stability of Corrole Complexes with Manganese, Copper, and Zinc in Environments Based on Acetic and Sulfuric Acids¹

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Abstract—Complexes of some *meso*- and *undeca*-substituted corroles with manganese, copper, and zinc are synthesized. Their stability in protolytic dissociation processes studied using spectroscopy methods increases for *meso*-triphenylcorrole (**I**) complexes in the following series of metals: Zn < Mn < Cu. The stability of copper complexes in the HOAc–H₂SO₄ environment increases after electron–donor substitution of molecules in the series: Cu(*ms*-Ph)₃Cor (**Ib**) > Cu(*ms*-4-OCH₃Ph)₃Cor (**IIIb**) ≈ Cu(β-Br)₈(*ms*-Ph)₃Cor (**IVb**) > Cu(*ms*-4-NO₂Ph)₃Cor (**IIIb**). Contrariwise, the dissociation rates of manganese corroles increase with increasing electron-donating properties of the substituents in the macrocycle: **IVb** < **IIIb** < **Ia** < **IIa**. Dissociation of metalcorroles is accompanied by donor-acceptor and acid–base interactions, as well as by intramolecular redox processes, to result in low selectivity of dissociation and formation of side products. The dissociation scheme of corrole complexes with mixed-valence *d* metals was proposed for the first time.

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Corroles (H₃Cor, compounds **I–IV**) form a unique family of tetrapyrrolic macrocyclic ligands that are structurally similar to porphyrins (H₂P). The contraction of the coordination cavity after one *meso*-methyl bridge was removed from the H₂P structure, electron density redistribution in the macrocycle, and the emergence of the third intracyclic NH proton makes the properties of H₃Cor and H₂P ligands significantly differ [1–3].

Corroles, which are usually used as metal complexes (MCor, compounds **Ia–IVa**, **Ib–IVb**, **Ic**) exhibit pronounced catalytic properties and show high promise for use in energy engineering and medicine, which places these porphyrinoids among the most popular research objects [1, 4, 5].

Dissociation of metalcorroles (**1**) in proton-donating environments is an important method to evaluate the chemical stability of complexes; in some cases, it is the only way to obtain the corresponding metal-free compounds (e.g., ligand **IV**) [6].



Despite the fact that the release of unbound corrole from its metal complex can be accompanied by ligand

oxidation to *iso*-corrole and other fluorine-like molecules, attempts at performing dissociation of corrole complexes have recently been made [6]. However, neither quantitative kinetic data nor mechanisms of this reaction have been reported [3].

In order to find the general trends of disintegration of MCor, a spectral kinetic study was performed into the dissociation of complexes of *meso*-phenyl-substituted corroles **I–IV** with manganese in the systems based on acetic acid (HOAc) and sulfuric acid (H₂SO₄) and conditions were selected for converting copper complexes in the HOAc–H₂SO₄ system and zinc complexes in the C₆H₆–HOAc environment.

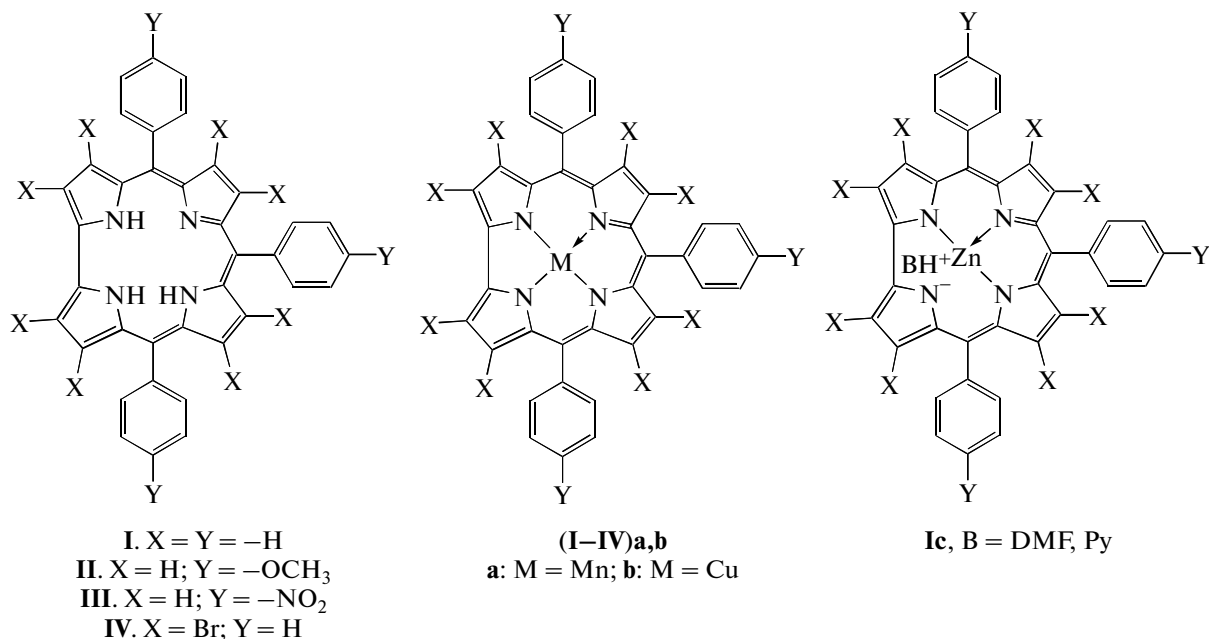
EXPERIMENTAL

Ligands **I–III** were synthesized using the procedures described earlier [7, 8].

The corrole complexes with manganese (**Ia–IIIa**) [9], copper (**Ib–IIIb**) [10], and zinc (**Ic**) [11] were prepared via complexation of the corresponding ligand with a tenfold molar excess of metal acetate in the *N,N*-dimethylformamide (DMF) environment followed by chloroform extraction of the product. The reaction of copper complex formation ends while the reagents are mixed at room temperature, whereas the formation of MnCor requires refluxing the reaction mixture for 15 min and the formation of ZnCorH requires heating the mixture at 60°C for 1.5 h.

[†] Deceased.

¹ On the occasion of 85th anniversary of Boris Dmitrievich Berezin (1929–2012), full member of the Russian Academy of Natural Sciences, Professor, Honored Scientist of Russia, awardee of the USSR State Award (1987) and the Russian Federation Government Award (2004).



β -Octabromo-*meso*-triphenylcorrole complexes with copper and manganese (**IVa**, **IVb**) [6, 7] were synthesized by direct bromination of β -unsubstituted complexes **Ia** or **Ib** in a 30-fold excess of bromine in chloroform (CHCl₃) followed by binding the releasing HBr to pyridine. The products were purified by silica gel column chromatography with CHCl₃ used as an eluent. The yield of compounds **IVa** and **IVb** is ~ 25%; the yield of compounds **Ia-IIIa**, **Ib-IIIb**, and **Ic** is 60–80%.

The structures of the resulting compounds were verified by ¹H NMR spectra and electronic spectroscopy data. Proton nuclear magnetic resonance (¹H NMR) spectra were recorded on an Avance 500 spectrometer (Bruker) with the operating frequency of 500 MHz at 303 K in CDCl₃. The electronic adsorption spectra (EAS) and the kinetics of reaction (1) were recorded on a Shimadzu UV 1800 spectrophotometer.

Organic solvents were additionally purified according to recommendations [12]. Acetic acid (HOAc, pure grade) was twice frozen and twice thawed, boiled with the calculated amount of acetic anhydride, and distilled on a fractionation column; the 117.5–118.0°C fraction was collected. Anhydrous sulfuric acid was prepared from a commercially available H₂SO₄ sample (pure grade) and 15% oleum; the concentration was monitored conductometrically and densitometrically ($\rho = 1.8384$).

The kinetics of dissociation reaction (1) for complexes **Ia-IVa** was recorded spectrophotometrically in the HOAc–H₂SO₄ environment. Equal volumes of the CHCl₃ solution of MCor complex with the known concentration prepared in advance were placed in test tubes; the solvent was evaporated. The dry residue of metal corrole was completely dissolved in the calcu-

lated amount of HOAc; the HOAc–H₂SO₄ mixture with the known concentrations of components was then added. The mixture was placed in the spectrophotometer cell holder and the change in absorbance at the operating wavelength λ_{exp} was measured after temperature-controlled exposure. The inaccuracy of temperature measurement was less than 0.1°C. Reaction (1) took place when one of the reagents was in a significant excess, which allows one to describe it with the pseudo-first-order kinetic equation

$$-dC/d\tau = k_v C_{\text{MnCor}}^n C_{\text{HX}}^n = k_{\text{eff}} C_{\text{MnCor}}^n \quad (2)$$

The order of reaction (1) with respect to metal complex, n , was always unity, as evidenced by the strictly linear dependences $\ln(C_0/C) = f(\tau)$ (Fig. 1). Effective reaction rate constants (k_{eff} , s⁻¹) were calculated using Eq. (3). The energy of activation (E_a , kJ/mol) and entropy of activation (ΔS^\ddagger , J/(mol K)) were calculated using Eqs. (4) and (5), respectively. The order of the reaction with respect to solvated proton H_{Solv}⁺ was determined graphically from $\log(k_{\text{eff}}) = f(H_0)$ (Fig. 1), where the current acidity function H₀ in the HOAc–H₂SO₄ system was calculated from experimental data [13]. The kinetic parameters of reaction (1) are listed in the table.

$$k_{\text{eff}} = \frac{1}{\tau} \ln \frac{C_0}{C\tau} = \frac{1}{\tau} \ln \frac{A_0 - A_\infty}{A_\tau - A_\infty}, \quad (3)$$

$$E_a = 19.15 \frac{T_1 T_2}{T_2 - T_1} \log \frac{k_2}{k_1}, \quad (4)$$

$$\Delta S^\ddagger = 19.15 \log k^{298} + \frac{E_{\text{avg}} \pm E_{\text{err}}}{298} - 253.22. \quad (5)$$

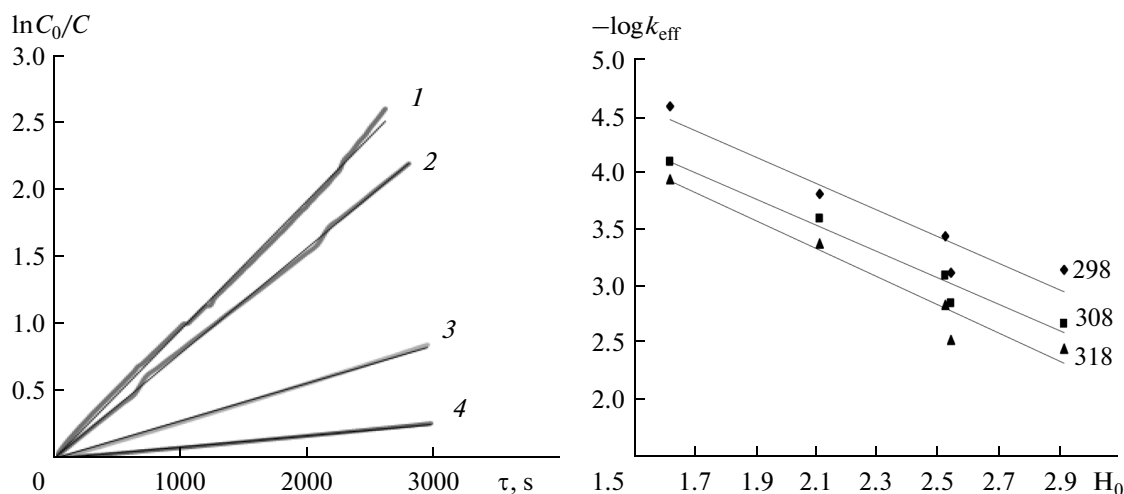
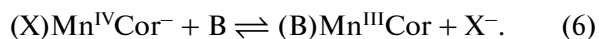


Fig. 1. $f(\ln C_0^{MCor}/C^{MCor}) = f(\tau)$ curves for the dissociation reaction of complex **IIa** in the HOAc–H₂SO₄ system at $T = 298$ K ($C_{H_2SO_4}$, mol/L): (1) 0.296; (2) 0.148; (3) 0.074; (4) 0.029 (left-hand panel) and the logarithmic dependence of the effective rate constant k_{eff} of reaction (1) on the Hammett acidity function H_0 in the HOAc–H₂SO₄ system ($\tan \alpha = 1.16$ – 1.25) at 298, 308, and 318 K (right-hand panel).

RESULTS AND DISCUSSION

Metalloporphyrins exist in solutions in extra coordinated ((L)MCor) and uncoordinated (MCor) forms. Metals that can change their valence (e.g., manganese) in these complexes typically can acquire a certain valence depending on the type of extra ligand (L), on whether it is a charged ligand (X^-) or an electron-donating molecule (B) (6). In this case the ligand H_3Cor is referred to as having a non-innocence effect [3, 14, 15], since there is an uncertainty in the metal oxidation state in MCor as it forms ligand-localized radical species. The H_3Cor macrocycle exhibits stronger electron-donating properties compared to porphyrins (H_2P), thus resulting in stabilization of metals in high oxidation states by these ligands [1–10]. Substitution of the X^- ligand at high concentrations of B, e.g., DMF (6–10 mol/L), in MCor is described by equilibrium (6) and characterized by drastic changes in the EAS [3].

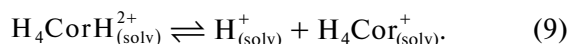
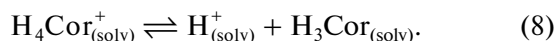
Similar equilibrium is also observed for copper corrole complexes (7); however, since the metal does not tend to coordinating extra ligands, it is almost independent of the solvent nature and the EAS of the two species are virtually identical.



Equilibrium (7) shifts leftward at room temperature, toward the copper(III) complex with a neutral ligand. This fact shows agreement with the literature data reporting the absence of signals from the CuCor radical species in the electron paramagnetic resonance (EPR) spectra and diamagnetic properties of CuCor

(¹H NMR signals at 7–8 ppm) as opposed to copper(II) porphyrin complexes [1, 10]. The ¹H NMR spectra of paramagnetic MnCor belong to a broad range of chemical shifts δ from –42 to +34 ppm.

Solvoprotolytic dissociation of metalloporphyrins (MPs) (dissociation induced by the solvated proton H_{Solv}^+ [16]) gives rise to a protonated ligand and a metal salt (1). It has been believed for a long time that dissociation of corrole complexes (MCor) to an unbound ligand is fundamentally infeasible [1, 6]. This opinion was caused by the fact that the formation of corrole mono- (H_4Cor^+ , 8) or dicationic (H_4CorH^{2+} , 9) caused by the interaction of acids with some of their metal complexes is either observed extremely rarely or is unobserved at all, while the absorption spectra of the products of treating MCor with an acid correspond to neither the EAS of the ligand nor any of its protonated species (Fig. 2).



Manganese corroles (compounds **Ia–IVa**) are the rare example of MCor complexes whose electronic absorption spectra of the dissociation products coincide with the EAS of the corresponding dicationic (Figs. 2, 3), which indicates that reaction (1) of these compounds is distinguished by a high degree of selectivity in the HOAc–H₂SO₄ system. The kinetic stability of *meso*-substituted manganese corroles considerably depends on the nature of substituents in phenyl rings

Kinetic parameters of dissociation reactions of manganese complexes of *meso*-substituted corroles and porphyrins in the HOAc–H₂SO₄ system, $C_{\text{MCoR}} = 4 \times 10^{-5}$ mol/L

Complex	C _{H₂SO₄} , mol/L	H ₀	T, K	$k_{\text{eff}} \times 10^3, \text{c}^{-1}$	$E_a, \text{kJ/mol}$	$\Delta S, \text{J/(mol K)}$
(Cl)Mn(<i>ms</i> -Ph) ₄ P [17]	3.00	−0.76	298	0.0005 ± 0.0003	80 ± 2	−105 ± 4
	4.00	−1.07		0.00047 ± 0.00003	105 ± 1	−22 ± 2
	5.00	−1.57		0.0031 ± 0.0006	100 ± 4	−30 ± 10
	6.61	−1.74		0.087 ± 0.005	97 ± 5	−3 ± 16
	7.13	−1.85		0.14 ± 0.01	100 ± 7	11 ± 24
	7.85			0.36 ± 0.02	67 ± 9	−93 ± 13
	Mn(<i>ms</i> -Ph) ₃ Cor, Ia $\lambda_{\text{exp}} = 601 \text{ nm}$	0.19	−0.76	298	0.026 ± 0.003	58 ± 20
0.46		−1.07		0.15 ± 0.04	40 ± 1	−193 ± 2
0.89		−1.57		0.37 ± 0.03	55 ± 4	−135 ± 13
1.31		−1.74		0.76 ± 0.06	54 ± 3	−132 ± 10
1.70		−1.85		0.72 ± 0.06	63 ± 14	−102 ± 47
3.00				1.43*		
4.00				1.93*		
Mn(<i>ms</i> -4-MeOPh) ₃ Cor, IIa $\lambda_{\text{exp}} = 650 \text{ nm}$	0.03	−0.67	298	0.09 ± 0.01	68 ± 7	−81 ± 24
			308	0.14 ± 0.01		
			318	0.27 ± 0.05		
	0.07	−1.10	298	0.28 ± 0.01	60 ± 3	−110 ± 8
			308	0.99 ± 0.10		
			318	1.47 ± 0.05		
	0.15	−1.55	298	0.85 ± 0.09	64 ± 20	−158 ± 55
			308	1.79 ± 0.07		
			318	3.92 ± 0.10		
	0.29	−1.83	298	1.10 ± 0.09	46 ± 5	−177 ± 16
308			2.34 ± 0.06			
318			6.17 ± 0.01			
4.00			15.28*			
Mn(<i>ms</i> -4-NO ₂ Ph) ₃ Cor, IIIa $\lambda_{\text{exp}} = 460 \text{ nm}$	2.50	−3.73	298	0.140 ± 0.007	59 ± 2	−129 ± 4
			308	0.312 ± 0.007		
			318	0.625 ± 0.013		
	2.83	−3.91	298	0.233 ± 0.034	49 ± 1	−158 ± 4
			308	0.454 ± 0.016		
			318	0.816 ± 0.060		
	3.40	−4.15	298		75**	
308			0.586 ± 0.003			
318			1.475 ± 0.007			
3.99	−4.44	298	0.420 ± 0.013	57 ± 7	−126 ± 21	
		308	0.785 ± 0.053			
		318	1.802 ± 0.016			
Mn(β-Br) ₈ (<i>ms</i> -Ph) ₃ Cor, IVa $\lambda_{\text{exp}} = 730 \text{ nm}$	2.01	−3.47	298	0.081 ± 0.006	60 ± 5	−325 ± 4
			308	0.198 ± 0.006		
			318	0.376 ± 0.013		
	3.14	−4.04	298	0.183 ± 0.008	53 ± 4	−319 ± 4
			308	0.345 ± 0.028		
			318	0.712 ± 0.031		
	4.07	−4.46	298	0.252 ± 0.010	72 ± 1	−314 ± 5
308			0.643 ± 0.015			
318			1.570 ± 0.115			

* Obtained by extrapolation.

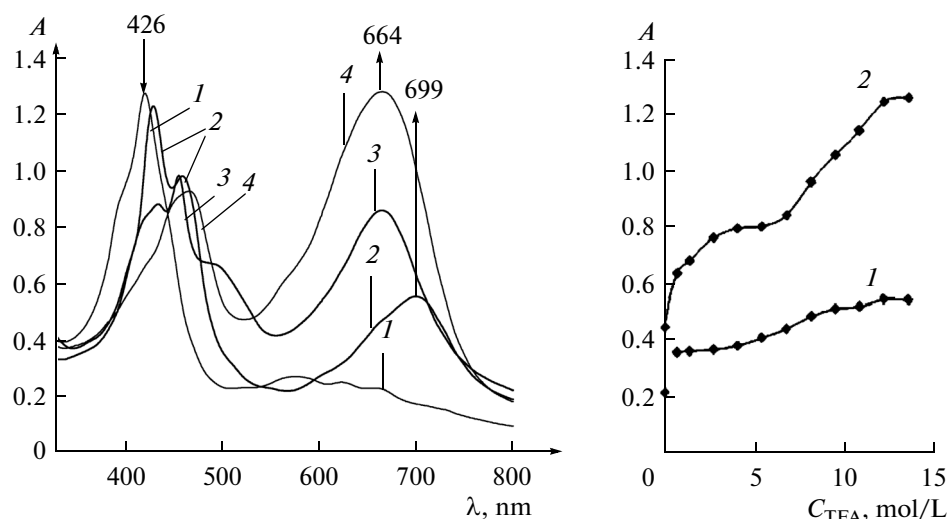
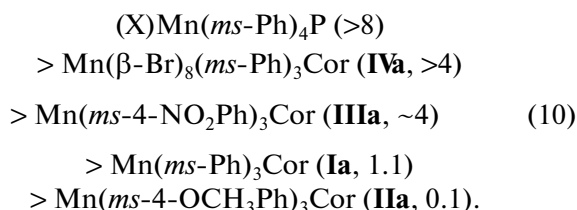


Fig. 2. Absorption spectra of compound **II**: (1) ligand H_3Cor ; (2) monocation $\text{H}_4\text{CorH}^{2+}$; (3) MeO-protonated monocation; (4) dication $\text{H}_4\text{CorH}^{2+}$ (left-hand panel) and titration curves for compound **I** (1) and **II** (2) (right-hand panel) in the MeCn–TFA system.

and β -positions of the macrocycle; it decreases in the series of complexes as follows² ((10), table):



Thus, dissociation of $\text{Mn}(\text{ms-4-NO}_2\text{Ph})_3\text{Cor}$ (**IIIa**) occurs in the environment under study at a rate of $\sim 5 \times 10^{-4} \text{ s}^{-1}$ in 4 M H_2SO_4 ; dissociation of $\text{Mn}(\text{ms-Ph})_3\text{Cor}$ (**Ia**) occurs in the presence of 1.1 M acid; while only 0.1 M H_2SO_4 is needed to decompose the most π -electron-excessive $\text{Mn}(\text{ms-4-MeOPh})_3\text{Cor}$ complex (table). Dissociation of complex **IIa** can occur very slowly even in glacial HOAc. Eight β -bromo substituents have a more pronounced accepting effect on the macrocycle compared to the three nitro groups at *para* positions of phenyl rings (table).

The comparison of the effective constants k_{eff}^{298} (3) obtained by extrapolation of the experimental values (table) to $C_{\text{H}_2\text{SO}_4} = 4 \text{ mol/L}$ indicates that addition of π -electron-donating substituents ($-\text{OCH}_3$) at the *para*-position of phenyl rings of corrole molecule **Ia** reduces the stability of $\text{Mn}(\text{ms-4-MeOPh})_3\text{Cor}$ metal complex eightfold, while the electron-accepting substitution by nitro groups in the $\text{Mn}(\text{ms-4-NO}_2\text{Ph})_3\text{Cor}$ molecule stabilizes it by almost 4.5 times at $C_{\text{H}_2\text{SO}_4} = 4 \text{ mol/L}$ compared to the unsubstituted complex. A similar effect of

² The H_2SO_4 concentration (mol/L) required to provide occurrence of reaction (1) with the rate constant $k_{\text{eff}} \sim 5 \times 10^{-4} \text{ s}^{-1}$ is given in parentheses.

phenyl substituents on the stability of corrole–manganese(III) complexes is observed for porphyrins. Thus, *p*-methoxy substitution in a manganese–tetraphenylporphyrine $(\text{AcO})\text{Mn}(\text{ms-Ph})_4\text{P}$ molecule reduces the stability of the complex almost 20-fold [17].

The stability of $\text{Mn}(\text{ms-Ph})_3\text{Cor}$ in 3 M H_2SO_4 is almost 3000 times as low as that of a metalloporphyrin having a similar structure, $(\text{Cl})\text{Mn}^{\text{III}}\text{TTPP}$. Thus, while $(\text{Cl})\text{Mn}^{\text{III}}\text{TTPP}$ dissociates in the HOAc– H_2SO_4 environment at $C_{\text{H}_2\text{SO}_4} = 3.00\text{--}7.85 \text{ mol/L}$ with $k_{\text{eff}} = (0.05\text{--}36.0) \times 10^{-5} \text{ s}^{-1}$ [14], $\text{Mn}(\text{ms-Ph})_3\text{Cor}$ decomposes in the range of concentrations as low as 0.19–1.70 M H_2SO_4 ($k_{\text{eff}} = (2.6\text{--}72.0) \times 10^{-5} \text{ s}^{-1}$) (table).

Protonated acetic acid H_2OAc^+ acts as an active species in the HOAc– H_2SO_4 environment [17]; the order of reaction (1) with respect to it at the limiting stage is close to unity (0.97–1.25 for compounds **Ia** and **IIa**) and 0.55–0.90 for **IIIa** and **IVa** according to the $\log(k_{\text{eff}}) = f(H_0)$ relationships (Fig. 1). Thus, one can say that the dissociation mechanisms of the manganese corroles in the HOAc– H_2SO_4 system are similar when $C_{\text{H}_2\text{SO}_4}$ is in the range from 0.03 to 4.10 mol/L. For complexes of variable-valence metals (copper and manganese), this is a complex process that involves both coordination and acid–base interactions as well as redox stages [11]. Based on the bimolecular nature of the limiting stage, we can assume that the dissociation of manganese corroles starts with the rapid reversible stage of protonation of inner-cyclic tertiary nitrogen ($=\text{N}-$) and simultaneous attachment of the acid anion via the acidprotolytic mechanism [16, 18] involving $\text{M} \leftarrow \text{N}^{22}$ coordination bond rupture (11). The product of this stage is spectrally observed as a bathochromic shift of the Soret band relative to the EAS in HOAc (Fig. 4).

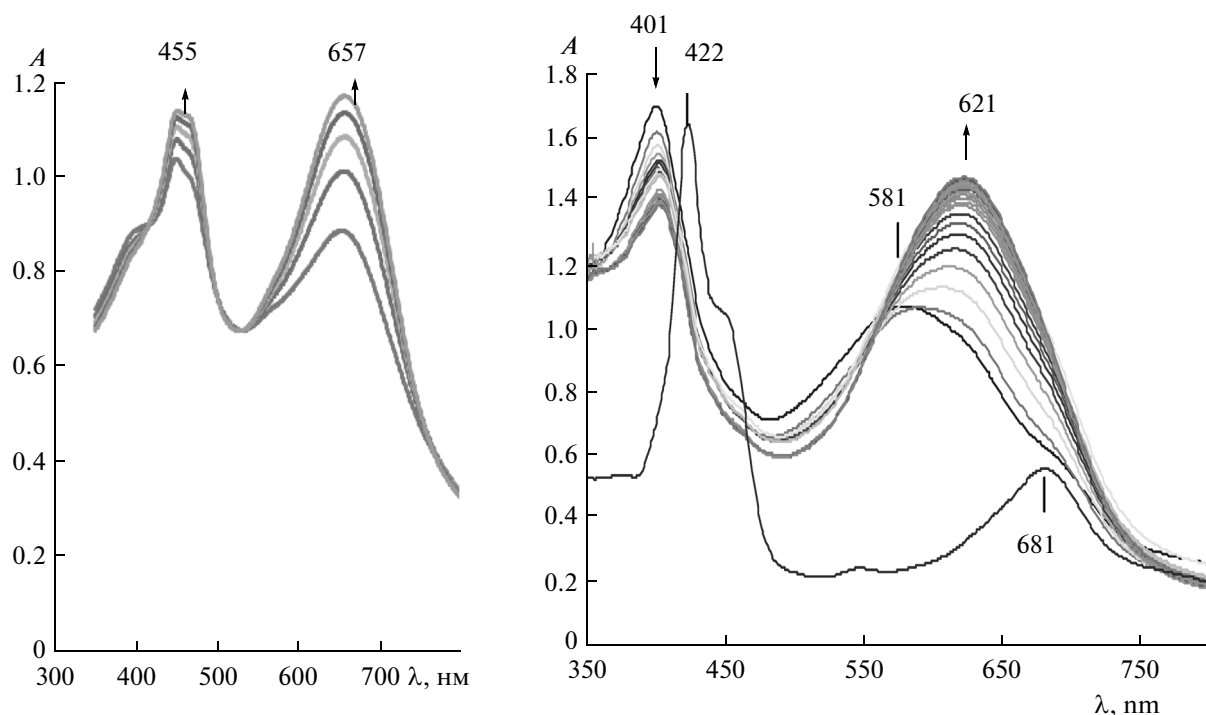
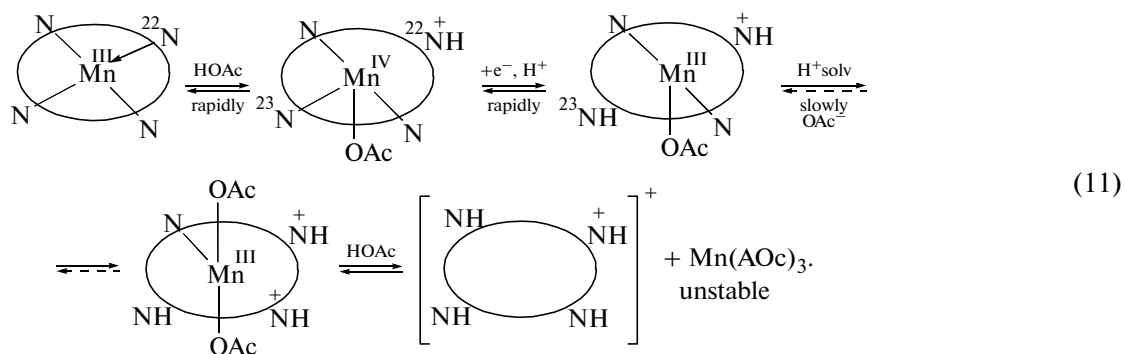
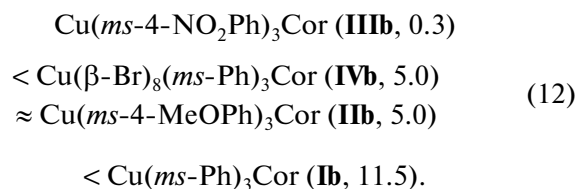


Fig. 3. Evolution of the EAS during dissociation of the Mn(*ms*-4-MeOPh)₃Cor complex (**IIa**) in the HOAc–H₂SO₄ system ($C_{\text{H}_2\text{SO}_4} = 0.45 \text{ mol/L}$, $\Delta\tau = 60 \text{ s}$) (left-hand panel) and Zn(*ms*-Ph)₃Cor (**Ic**) in the C₆H₆-HOAc environment ($C_{\text{HOAc}} = 2.6\text{--}7.9 \text{ mol/L}$, $T = 298 \text{ K}$) (right-hand panel, the spectrum of the ligand in 8 M HOAc in benzene is given for comparison).



Equilibrium (6) in an acidic environment strongly shifts to the left; (X)Mn^{IV}Cor participates in reaction (1). Protonation of the tertiary N atom promotes the occurrence of the subsequent stage of Mn^{IV} ↔ Mn^{III} reduction that takes place in an acidic environment and involves the rupture of the N²³–M bond (11). This bond is the most labile one as it is formed upon the dissociation of the most protonated N²³–H bond that is prone to form H-associates with weak electron donors [3, 19, 20]. The ⁵C- or ¹⁰C-protonation of one of *meso*-bridges of (X[–])MCor molecules is the limiting stage in the HOAc–H₂SO₄ environment; this stage results in the rupture of another (N–M) covalent bond. The resulting intermediate is unstable and easily dissociates in this environment giving rise to the [H₄CorH]²⁺ ligand (which is usually double-protonated).

The H₂SO₄ concentration required to disintegrate copper corrole complexes in the HOAc–H₂SO₄ environment (as opposed to manganese corrole complexes) increases as electron–donor substitution of the macrocycle occurs:³



³ C_{H₂SO₄} (mol/L) at which the dissociation is completed is given in parentheses.

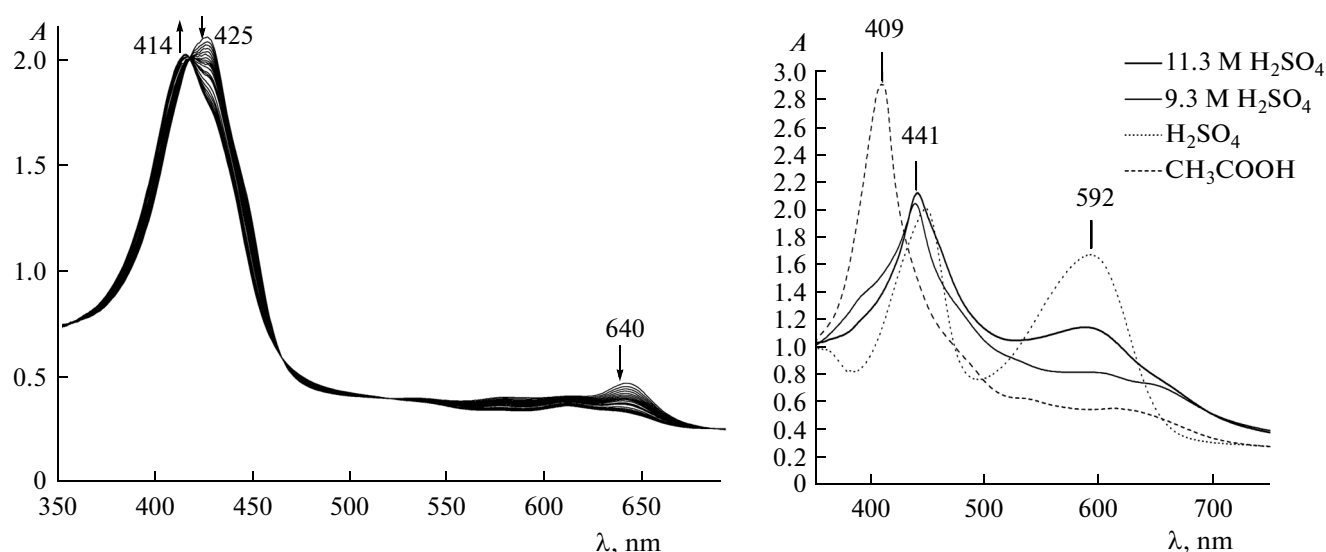


Fig. 4. Evolution of the EAS during formation of complex **Ib** in DMF at 298 K, $C_{\text{H}_3\text{Cor}} = 4 \times 10^{-5}$ mol/L, $C_{\text{Cu}(\text{OAc})_2} = 5.5 \times 10^{-5}$ mol/L, $\tau = 30$ s (left-hand panel); the absorption spectra of compound **Ib** in acetic and sulfuric acids and their mixtures (right-hand panel).

In the series of analyzed complexes with copper, compound **Ib** ($\text{Cu}(\text{ms-Ph})_3\text{Cor}$) is distinguished by the highest stability. After H_2SO_4 is added to the HOAc solution of this complex, the Soret band in the EAS shifts bathochromically by more than 30 nm; the spectrum in the visible range changes negligibly. The solubility of the complex increases abruptly when sulfuric acid concentrations in the HOAc– H_2SO_4 system are higher than 11.5 mol/L; the complex is disintegrated very rapidly and a band at 592 nm appears in its EAS (Fig. 4). This behavior is likely to be caused by the high degree of reversibility of dissociation for copper corrole complexes [6]. The EAS of the reaction products weakly correlate with the spectra of protonated ligands (Fig. 2). The rates of CuCor formation are extremely high. Thus, the reaction is completed as soon as in 300 s at 298 K in DMF environment even at virtually equimolar ratio between H_3Cor and copper acetate ($(4\text{--}5.5) \times 10^{-5}$) (Fig. 4, left-hand panel). The dissociation product in this case is presumably a mixture of the dication and side-products (*iso*-corroles) [6].

The position of compound **Ib** in series (12) is attributed to the electron-accepting properties of the methoxy group protonated by H_2SO_4 molecule [3]. The equilibrium of protonation of compound **I** at methoxy groups is observed in the acetonitrile (MeCN)–trifluoroacetic acid (TFA) system at acid concentrations of ≤ 4 mol/L (Fig. 2), while the dissociation of complex **Ib** takes place at higher environment acidities (12).

The stability of the studied complexes of compound **I** in acidic environment decreases in the following series of metals: $\text{Cu} > \text{Mn} > \text{Zn}$. Thus, $\text{H}_3(\text{ms-Ph})_3\text{Cor}$ complex undergoes conversions even after

exposure to 2.0–8.0 M acetic acid in benzene at 298 K; the final spectrum (in 8 M HOAc) of the product corresponds to the EAS of neither H_3Cor nor H_4Cor^+ (Fig. 3).

The spectral changes accompanying the conversion of compound **Ic** consist in the reduction of the Soret band at 401 nm in intensity and the increase in the only band at 581 nm and its bathochromic shift to 621 nm. The triphenylcorrole monocation H_4Cor^+ existing in the acidity range under analysis has bands at 422, 452, and 681 nm (Fig. 3). The EAS of the dissociation products of complex **Ic** in H_2SO_4 environment is close to that of $[\text{H}_4(\text{ms-Ph})_3\text{CorH}]^{2+}$ dication (449 and 600 nm, respectively); however, the intensity of the Soret band in this case is extremely high; furthermore, the dication cannot be formed at such a low acidity [3]. The conversion of the zinc complex of compound **I** is steady-state ($\text{p}K = 0.52$); the tangent of the function $\log(\text{Ind}) = f(\log C_{\text{HOAc}})$ is close to three. Unfortunately, the range of concentrations at which the conversion of **Ic** takes place does not allow one to take into account the acidity function H_0 in the $\text{C}_6\text{H}_6\text{--HOAc}$ system to determine the actual number of HOAc molecules participating in the reaction. The case of steady-state dissociation was previously detected in the $\text{C}_6\text{H}_6\text{--HOAc}$ system for the labile zinc complex with N-methyl-substituted porphyrinoid [21]; however, it decomposed giving rise strictly to protonated forms of the $\text{H}(\text{N-Me})\text{TPP}$ ligand. For the sake of comparison, the $\text{H}_2(\text{ms-Ph})_4\text{P}$ zinc complex is a relatively stable compound in the environment under study; it slowly dissociates only in glacial HOAc ($k_{\text{eff}}^{298} = 0.26 \times 10^{-3} \text{ s}^{-1}$) [16].

In summary, metallocorroles are distinguished by high degrees of specificity as they stabilize the unusual metal oxidation states via the formation of ligand-localized radical species, which significantly impedes selective dissociation of these complexes.

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