ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 4, pp. 737–744. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © N.M. Berezina, Vu Thi Thao, D.R. Karimov, R.S. Kumeev, A.V. Kustov, M.I. Bazanov, D.B. Berezin, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 4, pp. 661–669.

Synthesis and Properties of β-Brominated Metal Complexes of *meso*-Triphenylcorrole

N. M. Berezina[a], Vu Thi Thao[a], D. R. Karimov[a], R. S. Kumeev[b], A. V. Kustov[b], M. I. Bazanov[a], and D. B. Berezin[a]

[a] *Ivanovo State University of Chemistry and Technology, pr. Sheremetevskii 7, Ivanovo, 153000 Russia*
e-mail: sky_berezina@rambler.ru

[b] *G.A. Krestov Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, Russia*

Received May 14, 2013

Abstract—Spectral properties and chemical stability of Mn(III), Mn(IV), Fe(III), Fe(IV), and Cu(III) complexes of β-octabromotriphenylcorrole [(β-Br)$_8$(*ms*-Ph)$_3$Cor], synthesized from β-unsubstituted compounds by their reaction with molecular bromine, were studied. Cyclic voltammetry, electron microscopy, and X-ray spectral microanalysis were used to obtain electrochemical characteristics of metal corroles M(β-Br)$_8$(*ms*-Ph)$_3$Cor and gain insight into the surface texture of active catalysts on the basis of metal corroles. The electron-acceptor β-bromine substitution in the MCor macrocycle shifts the equilibrium in electron-donor solvents to lower oxidation states of the metals and also stabilizes manganese and destabilizes copper complexes in the proton-donor medium HOAc–H_2SO_4. The electrocatalytic activity of the complexes in the reduction of molecular oxygen depends on the nature of the ligand and increases in the order Mn $\le$ Cu $\ll$ Fe in the case of β-octabrominated macrocycles. The character of distribution of active centers on the surface of the catalysts was established for the first time.

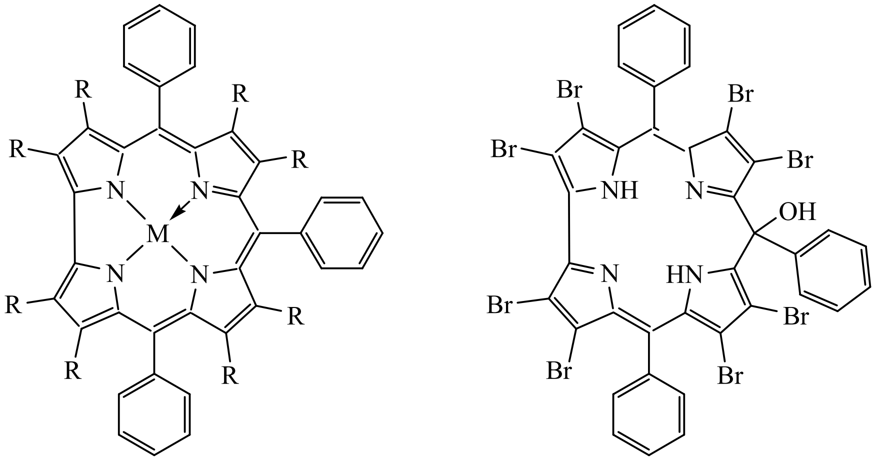
Keywords: metal corrole, bromination, electrochemical reduction, catalytic activity

DOI: 10.1134/S1070363214040239

The structural and electronic features of corroles H_3Cor and their metal complexes MCor (compounds **I–VI**) predetermine the versatile structures and high reactivity of such macrocycles and their potential efficiency as catalysts in redox reactions and chemical sensors in molecular recognition of small molecules [1]. The main interrelated characteristics of these compounds, which determine their unique features, including catalytic activity [1–3], are, first, ability of macrocycles to stabilize metals having unusual oxidation degrees in complexes with trianionic ligands, and, second, formation of ligand-localized radicals MCor due to the noninvolvement of ligand orbitals in coordination (*non-innocence effect*), which results in a certainly unclear oxidation state of metals in the resulting complexes [4, 5]. The metals atoms in such molecules are prone to redox reactions, and the complexes in themselves exhibit a high catalytic activity [1]. As previously shown [6, 7], exhaustive β-bromination of tetra-*meso*-phenylporphyrins (H_2P) substantially enhances their catalytic and electrocatalytic redox activity. Dodecasubstituted H_2P macroring experiences a strong out-of-plane distortion, which [6], along with the electron-acceptor effect of halogen substituents, was considered [6] as the main reasons of the enhanced catalytic activity. Unlike H_2P and MP, metal corroles (H_3Cor) are less sensitive steric effects of β- and *meso*-substituents in undecasubstituted molecules, both in crystal and in solution. This conclusion was based on the results of X-ray diffraction (XRD) analysis [8, 9] and quantum-chemical computations [4, 10, 11], as well as correlation of the electronic absorption spectra (UV-vis) and ^1H NMR spectra of β- (or *meso*-) and undecasubstituted (β-R = CH_3, Br, F) metal corroles (M = Co^{III}, Mn^{IV}, Cu^{III}, Fe^{IV}) [4, 12]. Thus, the fact that the spectra of polysubstituted corroles differ from those of β- or *meso*-substituted derivatives is likely to be largely explained by the electronic effects of β-substituents.

In the present work, aimed at analyzing the effect of β-substitution on the physicochemical properties of

Scheme 1.



I–VI **VII**

I: M = (DMF)Mn^{III}; R = H, **II**: M = (Cl)Fe^{IV}; R = H, **III**: M = Cu^{III}; R = H, **IV**: M = (Py)Mn^{III}; R = Br, **V**: M = (Cl)Fe^{IV}; R = Br, **VI**: M = Cu^{III}; R = Br.

macroheterocycles, we synthesized Mn^{III}, Fe^{IV}, and Cu^{III} complexes of β-octabromo-*meso*-triphenylcorrole (complexes **IV–VI**) and studied their spectral characteristics, stability in proton-donor media, and catalytic activity in the electrochemical reduction of molecular oxygen. The resulting data were compared with those for the corresponding β-unsubstituted complexes **I–III** [2] (Scheme 1).

Unlike metal porphyrins (MP), corrole ligands could not still be obtained from complexes by the dissociation reaction (1); H_3Cor could only be obtained from certain manganese(IV), iron(IV), and copper(III) complexes [11, 13]. This is associated with the fact that corroles stabilize metals in high oxidation states [14], and, therefore, MCor the dissociation can be accompanied by the oxidation of ligands into phlorin-type compounds (for example, isocorrole **VII**), or other molecules by the released metal ion [13].

$$M^{n+}\mathrm{Cor} + 3\mathrm{H}^{+}_{\mathrm{Solv}} \rightleftarrows \mathrm{H_3Cor} + \mathrm{M}^{n+}_{\mathrm{Solv}}. \qquad (1)$$

Bromination of a *meso*-triphenyl-substituted ligand H_3Cor, too, does not lead to the desired result, yielding isocorrole [9, 13]. Therefore, to synthesize undecasubstituted β-octabromotriphenylcorrole complexes **IV–VI**, we made use of an approach involving bromination of *meso*-triphenylcorrole complexes **I–III** by molecular bromine [reaction (2)] [13]. The individuality and purity of complexes **IV–VI** was confirmed by UV-vis and ^{1}H NMR [4, 11, 15, 16] and X-ray spectral microanalysis (Table 1, Figs. 1–3).

$$\mathrm{M}(ms\text{-Ph})_3\mathrm{Cor} \xrightarrow[\text{(2) Py}]{\text{(1) Br}_2,\ \text{CHCl}_3} \underset{\textbf{IV–VI}}{\mathrm{M}(\beta\text{-Br})_8(ms\text{-Ph})_3\mathrm{Cor}}. \qquad (2)$$

The UV-vis spectra of metal corroles **I–VI** in noncoordinating media (C_6H_6, $CHCl_3$) show a Soret band (385–445 nm) and weak absorption bands in the visible range. In electron-donor solvents (DMF, Py), the visible spectra of the metal complexes show well-defined *Q* bands at 535–670 nm for Cu^{III} and Mn^{III} corroles and 560–570 nm for iron corroles. The Soret and Q_{I} bands in the UV-vis spectra of undecasubstituted complexes, except for Fe^{IV} complexes, are shifted red with respect to those in the spectra of metal corroles **I–III** by 3–34 and 7–25 nm, respectively (Table 1).

Based on the abundant evidence on the state of metal porphyrins in coordinating solvents (Solv) [18, 19], it would be logical to suggest that the changes in the UV-vis spectra are associated with additional coordination of Solv with the metal atom [reaction (3)]. At the same time, extra coordination of metal porphyrins usually shifts their absorption maxima by no more than 5–20 nm, it gives rise to no electron transitions and takes place at low Solv concentrations. In the case of MCor, the structure of the absorption spectrum changes essentially (Fig. 1, Table 1), and, for example, when a noncoordinating solvent is replaced by an electron-donor one, changes in the spectra of manganese complexes **I** and **IV** are complete at the concentration of the electron donor of about 6 M.

Table 1. Electronic absorption spectra and X-ray spectral microanalysis data for complexes **I–VI**

Compound	Solvent	Soret band, nm (log ε)	λ_{III}, nm (log ε)	λ_{II}, nm (log ε)	λ_{I}, nm (log ε)	Br/M ratio
Cu(*ms*-Ph)$_3$Cor (**III**) [17]	$CHCl_3$	411 (4.92)	–	537 (3.74)	619 (3.51)	–
	DMF	431	–	535, 576	607, 776 w	
Mn(*ms*-Ph)$_3$Cor (**I**) [17]	$CHCl_3$	433 (4.57)	–	589 (3.54)	–	–
	DMF	401 (4.42), 436 (4.48), 462 sh (4.27), 494 (4.14)	–	574 (3.84)	652 (3.95)	
Fe(*ms*-Ph)$_3$Cor (**II**) [17]	$CHCl_3$	401 (4.56)	–	602 w (3.99)		–
	DMF	397 (4.61)	562 (4.19)	602 w (4.10)	728 w (3.92)	
Cu[(β-Br)$_8$(*ms*-Ph)$_3$Cor] (**VI**)	$CHCl_3$	445 (4.78)	–	522 sh (4.19)	642 w (3.88)	10.9
	DMF	437 (4.82)	–	537 w (4.12), 587 (4.12)	622 w (4.08)	
Mn[(β-Br)$_8$(*ms*-Ph)$_3$Cor] (**IV**)	$CHCl_3$	386 (4.63), 419 (4.63)	–	–	614 sh (3.94), 660 sh (3.81), 757 w (3.64)	9.8
	DMF	392 (4.57), 440 (4.63); 464 w (4.53), 497 (4.61)	–	556 w (4.31)	619 w (4.27), 669 (4.40)	
Fe[(β-Br)$_8$(*ms*-Ph)$_3$Cor] (**V**)	$CHCl_3$	386 (4.69)	–	560 w (3.95)	786 w (3.50)	8.0
	DMF	397 (4.65)	546 w (4.22)	567 (4.23)	770 w (3.94)	

$$\mathrm{MP} + n\mathrm{Solv} \rightleftarrows (\mathrm{Solv})_n\mathrm{MP}. \qquad (3)$$

In the case of corrole complexes with metals capable of undergoing redox reactions, formation of extra complexes or their dissociation is accompanied by a change in the valence state of the metal atom [11, 20]. Complexes M^{III}Cor with characteristic UV-vis spectra (Fig. 1b) are usually formed during synthesis via complex formation in electron-donor media (Solv = DMF, Py; M = Mn, Fe, Cu). Treatment of iron and manganese complexes with dilute solutions of acids (HOAc, HCl) results in a fast shift of the

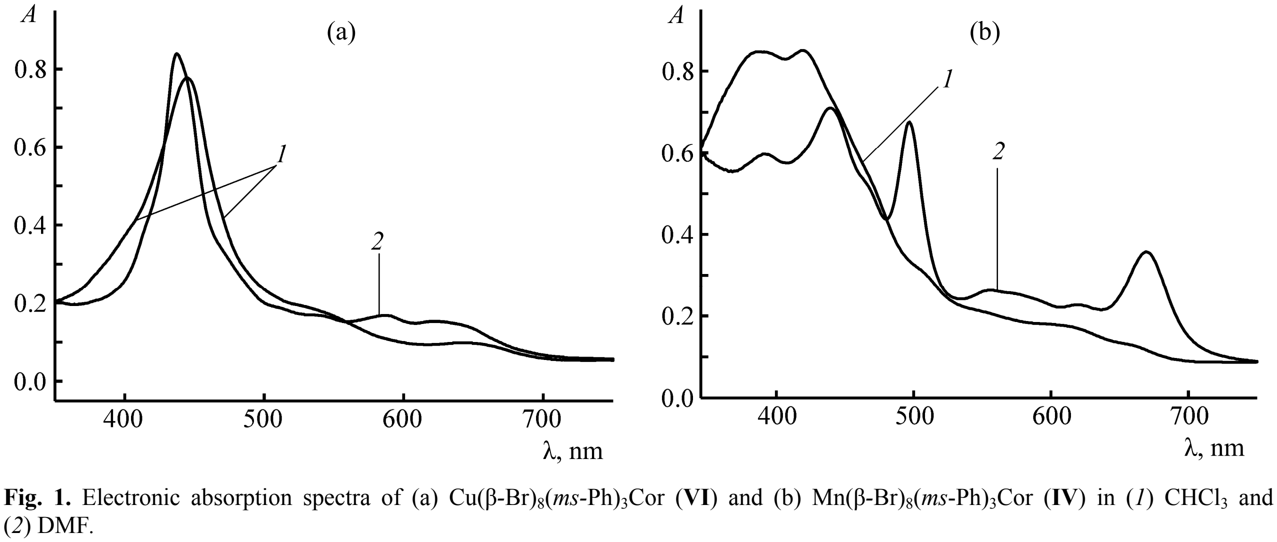


Fig. 1. Electronic absorption spectra of (a) Cu(β-Br)$_8$(*ms*-Ph)$_3$Cor (**VI**) and (b) Mn(β-Br)$_8$(*ms*-Ph)$_3$Cor (**IV**) in (*1*) $CHCl_3$ and (*2*) DMF.

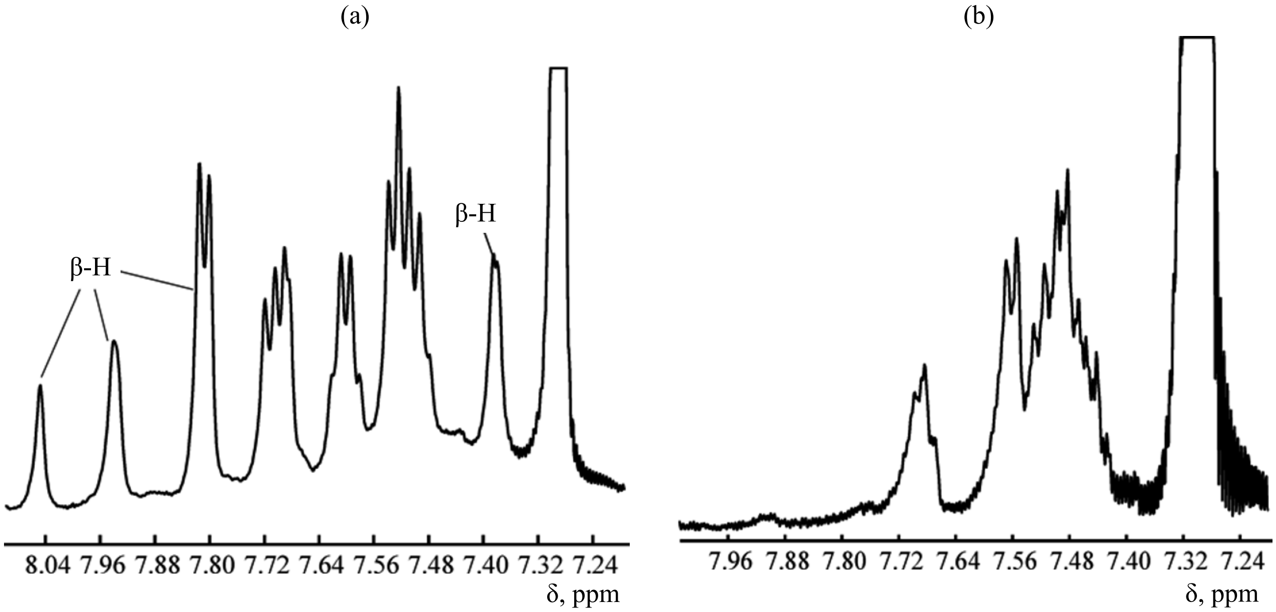


Fig. 2. Aromatic proton resonance region in the ^{1}H NMR spectrum of (a) Cu(ms-Ph)$_3$Cor (**III**) and (b) Cu(β-Br)$_8$(ms-Ph)$_3$Cor (**VI**) in CDCl$_3$, 298 K.

equilibrium (Solv)M^{III} $\rightleftarrows$ (X)M^{IV}, where X is the acid anion. The dissociation of extra complex (Solv)Mn^{III}Cor in weakly or noncoordination solvents, especially if the solvent is an acid and the medium contains its anions (CHCl$_3$), is a slow process, whereas Fe(III) complexes lose extra ligand Solv and undergo an intramolecular redox reaction (*non-innocence effect*) [4, 5] to form (Cl)Fe^{IV}Cor$^{-\cdot}$ already during chloroform extraction of the product from the reaction mixture [17]. The rate of this transformation is strongly dependent on the charge on the metal atom and is much lower in β-octabrominated complexes **IV** and **V** than in compounds **I** and **II**. The reverse process takes place in the course of titration of a solution of (X)M^{IV}Cor$^{-\cdot}$ in an inert solvent; in this case, the equilibrium constant is difficult to determine, because several processes occur concurrently. The mechanism of the process is, too, unknown. Apparently, the first, fast stage involves coordination of Solv, and then, at the limiting stage, cleavage of the X$^-$ anion takes place [reaction (4)].

$$(X^-)M^{IV}Cor^{-\cdot} + Solv \rightleftarrows (X^-)(Solv)M^{IV}Cor^{-\cdot}$$

$$\overset{-X^-}{\rightleftarrows} (Solv)M^{III}Cor. \qquad (4)$$

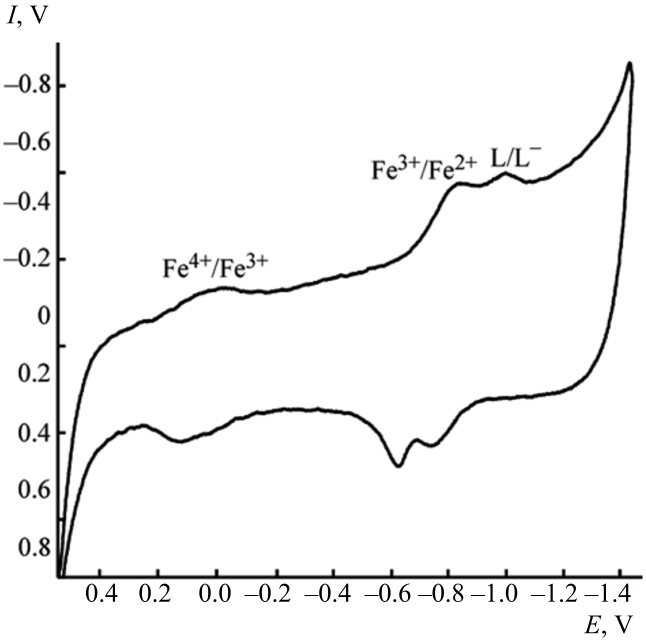


Fig. 3. Current–voltage curve for the electrode coated with (Cl)Fe^{IV}(β-Br)$_8$(ms-Ph)$_3$Cor$^{-\cdot}$ (**V**) in 0.1 M KOH (argon). Scan rate 0.02 V/s.

On solvent change, equilibrium (5) in complexes Cu^{III}Cor [4, 14] shifts only slightly, as evidenced by minor changes in the EAS spectrum of complex **III** (Table 1). With compound **VI**, the spectral pattern changes more essentially (Fig. 1a), and, therewith, eight electron-acceptor substituents stabilize the lowest valence state of the metal ions and the radical cation state of the ligand (*non-innocence effect*) [equilibrium (5)] [4, 5, 17]. It is unlikely that the spectral changes are associated with Solv extra coordination, because copper(II) does not tend to form octahedral complexes [7].

$$M^{III}Cor \rightleftarrows M^{II}Cor^{-\cdot}. \quad (5)$$

The spectral (^{1}H NMR) characteristics of corrole complexes **I–VI** were detected in $CDCl_3$ which stabilizes higher oxidation states of metals (Mn^{IV}, Fe^{IV}, and Cu^{III}; Mn^{IV} is formed only after prolonged storage of the solution). The ^{1}H NMR spectrum of copper complex **III** shows signals at 7.36–8.03 ppm in the region of phenyl and β-pyrrole proton resonance. The diamagnetism of compound **III** is evidence showing that the oxidation state of the metal is +3. At the same time, the corresponding copper(II) complexes with porphyrins are paramagnetic [7, 17]. The equilibrium between $Cu^{III}Cor$ and $Cu^{II}Cor^{+\cdot}$ in $CDCl_3$ at room temperature is almost completely shifted to $Cu^{III}Cor$, which agrees with published data [4, 13]. β-Octabromine substitution in copper *meso*-triphenyl-corrole complex **III** results in disappearance of the β-proton signals, while the *meso*-phenyl proton signals at 7.46–7.74 ppm are preserved (Fig. 2).

The ^{1}H NMR signals of paramagnetic Mn(IV) and Fe(IV) complexes **I** and **II** appear in a wide range of chemical shifts: from –42.3 to +33.9 ppm (**I**) and from–41.1 to +25.2 ppm (**II**). Usually the signals of complexes $(X)Fe^{IV}Cor^{-\cdot}$ with highly negative chemical shifts are assignable to β protons of the electron-excessive α,α-dipyrrole fragment and the signals with positive chemical shifts, to the *ortho* (and *para*) protons of the *meso*-phenyl rings. The ^{1}H NMR spectra of manganese complexes were not assigned completely [11]. β-Bromination of the macrorings results in disappearance of the pyrrole proton signals at –43.28 and 34 ppm in the spectrum of complex **IV** and of the upfield signals ($\delta < -10$ ppm) in the spectrum of compound **V**.

Further evidence for the composition of complexes **IV–VI**, in particular, with the aim of establish their β-bromination degree, we performed X-ray spectral measurements of active mixtures of catalysts [2] on the basis of these metal corroles. The results, even though the measurement error was fairly high (about 25%), showed that the M/Br ratio was ≥ 8 in all the complexes (Table 1).

Corrole complexes with *p* and *d* elements, like complexes with other macrocyclic aromatic ligands, show a high kinetic stability to dissociation [7] and dissociate exclusively in strongly proton-donor media [reaction (1)]. Unlike what proved possible with most MPs, in the case of MCor we could measure dissociation kinetics for Mn(IV) compounds which are rapidly formed, when $(Solv)Mn^{III}Cor$ are dissolved in acid mixtures [reaction (6)]. With $Cu^{III}Cor$, equilibrium (1) is shifted to its formation, and, therefore, dissociation normally takes place only in highly acidic media, and the complex can be formed again, when the acid solution is diluted with the aim to isolate products [13]. The state of iron corroles in acid solutions is still an open problem, and it is to be solved in separate research.

$$(Solv)M^{III}Cor + HX \rightleftarrows (X)M^{IV}Cor^{-\cdot} + Solv + H^+. \quad (6)$$

The spectral kinetic study of the dissociation of Mn(IV) and Cu(III) *meso*-phenyl-substituted corrole complexes **I** and **III** in $HOAc–H_2SO_4$ mixtures showed that the Cu(III) complex is more stable than the Mn(IV) complex. The H_2SO_4 concentration required for dissociation of $Cu^{III}Cor$ in the $HOAc–H_2SO_4$ medium in the case of the more electron-donor macrocycle **III** increases: 11.5 (**III**) > 5.0 (**VI**). No selective formation of protonated ligands H_4Cor^+ or $(H_4CorH)^{2+}$ from copper(III) complexes takes place under the action of acids. Evidence for this conclusion comes from the fact that the EAS spectra of the reaction products do not coincide with the spectra of corrole mono- and dications and are assignable to hydroxyphlorin structures **VII** formed by side oxidation reactions of the complexes [13].

The dissociation of $(X)Mn^{IV}Cor^{-\cdot}$ complexes **I** and **IV** in the $HOAc–H_2SO_4$ system results in selective formation of the dication H_4CorH^{2+}. Dissociation of *meso*-substituted manganese corroles, unlike what is characteristic of copper(III) complexes, is accelerated by electron-donor substituents. Comparison of the apparent rate constants of reaction (1), obtained by the extrapolation of their concentration dependence to $c(H_2SO_4)$ 4 M, provides evidence showing that electron-acceptor β-octabromine substitution in manganese corrole **IV** (k_{app}^{298} 0.252 × 10^{-3} s^{-1}) makes the metal complex about 7.5 times more stable than unsubstituted compound **I**. The same effect of substituents on stability was also observed in Mn(III) H_2P complexes [7, 21].

The high chemical and heat resistance of metal corroles [17], along with unique structural features, favor use of these compounds in catalysis. We estimated the electronic effect of multiple β substituents (R = Br) in metal corroles on their redox potential and activity

Table 2. Potentials of redox reactions ($E_{1/2}$, V) on electrodes coated with H_2P, H_3Cor, their β-octabromo derivatives, and metal complexes **I–VI** at the scan rate of 0.02 V/s

Compound	Process I $M^{4+} \leftrightarrow M^{3+}$			Process II $M^{3+} \leftrightarrow M^{2+}$			Process III $L \leftrightarrow L^{-}$			$E_{1/2}(O_2)$	Reerences
	E^{I}_{cat}, V	E^{I}_{an}, V	$E^{I}_{red/ox}$, V	E^{II}_{cat}, V	E^{II}_{an}, V	$E^{II}_{red/ox}$, V	E^{III}_{cat}, V	E^{III}_{an}, V	$E^{III}_{red/ox}$, V		
H_2(*ms*-Ph)$_4$P	–	–	–	–	–	–	–1.081	–0.968	–1.025	–0.275	[22]
Co(*ms*-Ph)$_4$P	0.130	0.260	0.200	–0.580	–0.480	–0.530	–1.210	–1.000	–1.110	–0.230	[22]
Co(β-Br)$_8$(*ms*-Ph)$_4$P	0.130	0.370	0.250	–0.870	–0.500	–0.690	–1.150	–0.920	–1.040	–0.160	[22]
H_3(*ms*-Ph)$_3$Cor	–	–	–	–	–	–	–1.088	–0.606	–0.847	–0.257	[2]
(DMF)Mn^{III}(*ms*-Ph)$_3$Cor (**I**)	–0.333	0.118	–0.108	–0.668	–0.569	–0.619	–1.095	–0.969	–1.033	–0.160	[2]
(Cl)Fe^{IV}(*ms*-Ph)$_3$$Cor^{-\cdot}$ (**II**)	–0.160	–0.075	–0.117	–0.875	–0.785	–0.830	–1.057	–0.605	–0.831	–0.122	[2]
Cu^{III}(*ms*-Ph)$_3$Cor (**III**)	–	–	–	–0.468	–0.309	–0.389	–1.106	–	–	–0.250	[2]
(Py)Mn^{III}(β-Br$_8$)(*ms*-Ph)$_3$Cor (**IV**)	0.292	0.410	0.351	–0.528	–0.481	–0.505	–1.048	–0.604	–0.826	–0.236	–
(Cl)Fe^{IV}(β-Br)$_8$(*ms*-Ph)$_3$$Cor^{-\cdot}$ (**V**)	–0.008	0.003	–0.005	–0.842	–0.743	–0.793	–1.029	–0.610	–0.820	–0.130	–
Cu^{III}(β-Br)$_8$(*ms*-Ph)$_3$Cor (**VI**)	–	–	–	–	–	–	–1.044	–0.602	–0.823	–0.226	–

in the electrochemical reduction of oxygen (Table 2) [23].

The electrochemical characteristics of undecasubstituted complexes **IV–VI**, as measured in 0.1 M aqueous KOH under argon, differ from those of β-unsubstituted compounds **I–III**. The potentials of [M(β-Br)$_8$(*ms*-Ph)$_3$Cor] in all the observed redox processes are shifted to positive values with respect to those for β-unsubstituted metal *meso*-triphenylcorroles [2] and β-octabromotetrphenylporphyrin complexes (Table 2) [22]. At the same time, β-octabromination in Co(*ms*-Ph)$_4$P, unlike what takes place in corroles, decreases the potentials of those redox processes that involve the ligand and not the metal (Table 2) [22], which may be associated with the spatial distortion of the macrocycle. The electrochemical reduction potential of metal corroles **IV–VI** is lower by 220–285 mV compared to structurally similar H_2P complexes (Table 2).

In terms of the metal complex electrocatalysis, the most important redox processes are those occurring at low potentials and involving catalyst metal centers [23]. Metal-centered redox processes were observed in Fe(β-Br)$_8$(*ms*-Ph)$_3$Cor (**V**) at $E_{red/ox}$ –0.005 V (Fe^{IV}–Fe^{III} reduction) and $E_{red/ox}$ –0.793 V (Fe^{III}–Fe^{II} reduction), like in unsubstituted complex **II** (Table 2). The first stage is characterized by a high degree of reversibility (Fig. 3). With Mn(β-Br)$_8$(*ms*-Ph)$_3$Cor in an alkaline solution (Table 2), we observed two reversible maxima corresponding the reductions Mn^{IV}–Mn^{III} (E^{cat} 0.351 V) and Mn^{III}–Mn^{II} (E^{cat} –0.505 V). In the case of Cu^{III}(β-Br)$_8$(*ms*-Ph)$_3$Cor, no Cu(III)–Cu(II) reduction was detected, even though in the β-unsubstituted copper(III) complex it is observed –0.389 V [2].

The electrochemical reduction order of metals (M^{III}–M^{II}) in β-unsubstituted complexes **I–III** parallels the order of dissociation rates of the complexes in the presence of the reducer $SnCl_2$ (Cu > Mn > Fe) [24, 25].

Upon saturation of the aqueous alkaline solution with molecular oxygen, the *I, E*-curves demonstrate a considerable rise of current in the potential range –(0.1–0.4) V, which is associated with the electrochemical reduction of O_2 on the catalyst-modified electrode surface (Table 2). The electrocatalytic activity of a sample is judged about by the half-wave reduction potential of molecular oxygen $E_{1/2}(O_2)$ [2, 22] (Table 2).Analysis of the $E_{1/2}(O_2)$ values for compounds **I–V** allows us to conclude that the β-bromination of complexes **I–III** to form undecasubstituted macrocycles does not always positively

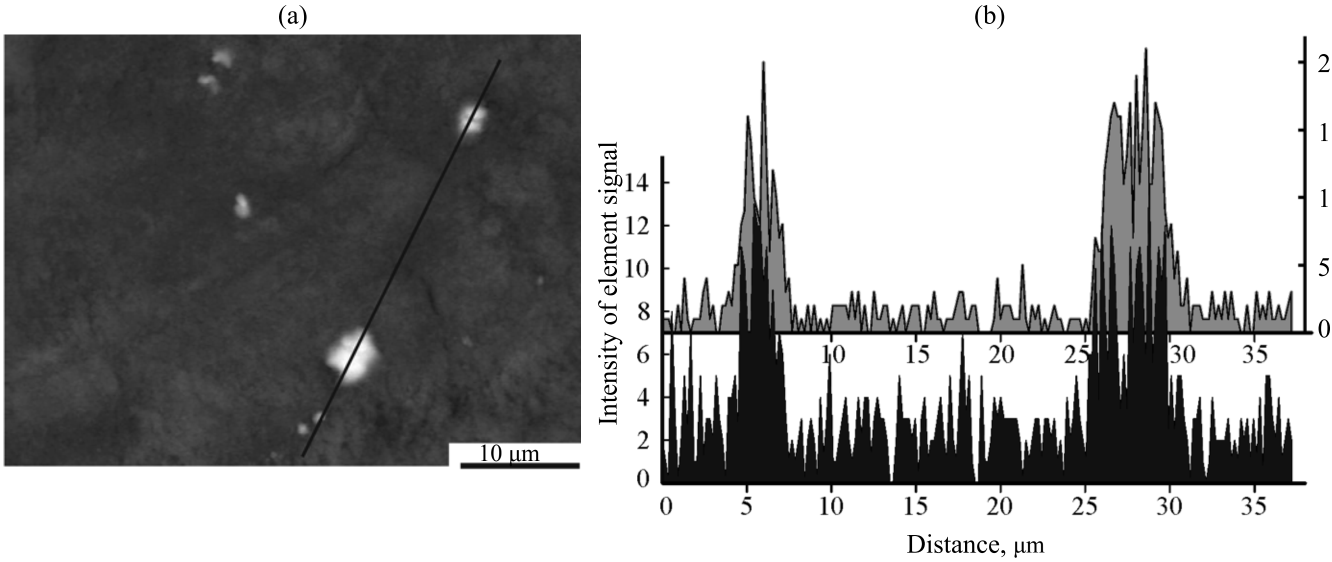


Fig. 4. (a) Microscopic image of the surface of the active catalytic mass on the basis of $(Cl)Fe^{IV}(\beta\text{-}Br)_8(\textit{ms}\text{-}Ph)_3Cor^{-\cdot}$ (**V**) and (b) scanning of its atomic composition along the line shown in the image: (on a dark backround) Fe signal and (on a light background) Br signal.

affect the electrocatalytic activity, unlike what occurs in MPs with a similar type of functional substitution (Table 2), which is consistent with the electron-acceptor properties of bromine substituents in the absence of the macrocycle distortion effect [2]. β-Bromination strongly increases the electrochemical reduction potential of oxygen $E_{1/2}(O_2)$ only in copper complex **VI**; in iron complex **V,** the $E_{1/2}(O_2)$ value remains unchanged, whereas in manganese complex **IV**, it, by contrast, strongly decreases. Thus, the electrocatalytic activity of tetrapyrroles **IV–VI** increases in the order Mn ≤ Cu < Fe. As previously mentioned, the activity order of metals in the electrochemical reducetion of oxygen varies depending on the nature of the ligand [23], which, indeed, was observed in the experiment.

We performed the first joint electron microscopy and X-ray spectral microanalysis study of active catalytic masses on the basis of metal corroles **I–VI** to show that the catalyst surface is non-uniform in atomic composition (Fig. 4). This is well seen in the microscopic image of the active mass of complex **V** (Fig. 4a). X-Ray spectral microanalysis, including scanning of the atomic structure of the surface along the line shown in the figure, showed that the metal corrole is primarily localized in granules 1–5 μm in diameter, that contain the most part of active catalytic centers, and the concentration of metal atoms between such centers is very low (Fig. 4b).

EXPERIMENTAL

The ^1H NMR spectra were run on an Avance-500 spectrometer (Bruker) at 500 MHz and 303 K. The electronic absorption spectra and kinetics of reaction (1) were measured on a Shimadzu UV1800 instrument. The microscopic images were obtained and analysis of surface composition of active catalytic masses was performed on a LEO 1455 VP scanning electron microscope (Carl Zeiss, Germany) with a SiLi detector for X-ray spectral microanalysis.

Manganese(III), iron(IV), and copper(III) β-octabromotriphenylcorroles **IV–VI** were synthesized by the procedure in [13]. To a solution of 55 mg (0.094 mmol) of complex **I, II**, or **III** in 25 mL of $CHCl_3$, a 30-fold excess of bromine in the solvent was added (10 mL). The reaction mixture was stirred for 1 h and 298 K, a solution of 3.4 mmol of pyridine in 10 mL of $CHCl_3$ was added and stirring was continued for an additional 1–2. The mixture was washed with sodium sulfite and water, the organic layer was separated, the solvent was evaporated, and the reaction product was purified by column chromatography on silica (eluent chloroform). Yield ca. 25%.

The dissociation kinetics of complex **IV** in the HOAc–H_2SO_4 medium [reaction (1)] was followed by spectrophotometry according to the procedure in [26]. The active catalytic masses on the basis of complexes

IV–VI were prepared, and their electrochemical and electrocatalytic study by cyclic voltammetry in 0.1 M KOH (chemical grade) was performed as described in [2]. The redox potentials [$E_{red/ox} = (E_{cat} + E_{an})/2$] were averaged over 5–6 runs, the relative error in the resulting values was no more than 3%.

Organic solvents [$CHCl_3$ (chemical grade), DMF and Py (analytical grade), and HOAc (pure grade)] and water were purified according to [27]. Anhydrous sulfuric acid was prepared from commercial H_2SO_4 (chemical grade) and 15% oleum with conductometric and densimetric (ρ 1.8384) concentration control.

ACKNOWLEDGMENTS

The work was financially supported by the Russian Foundation for Basic Research (project no. 12-03-97542-r_tsentr_a) and Optec LLC (Carl Zeiss).

REFERENCES

1. Aviv, I. and Gross, Z., *Chem. Commun.*, 2007, p. 1987.
2. Bazanov, M.I., Berezina, N.M., Karimov, D.R., and Berezin, D.B., *Russ. J. Electrochem.*, 2012, vol. 48, no. 9, p. 905.
3. Berezina N.M., Karimov D.R., Bazanov M.I., and Berezin D.B., *Izv. Vuzov, Ser. Khim. Khim. Tekhnol.*, 2013, vol. 56, no. 6, p. 37.
4. Wasbotten, I.H., Wondimagegn, T., and Ghosh, A., *J. Am. Chem. Soc.*, 2002, vol. 124, no. 27, p. 8104.
5. Stefanelli, M., Nardis, S., Tortora, L., Fronczek, F.R., Smith, K.M., Licoccia, S., and Paolesse, R., *Chem. Commun.*, 2011, p. 4255.
6. *The Porphyrin Handbook,* Kadish, K.M., Smith, K.M., and Guilard, R., Eds., New York: Acad. Press, 2000, vol. 1, p. 239.
7. Berezin, D.B., *Makrotsiklicheskii effekt i strukturnaya khimiya porfirinov* (Macrocycli Effect and Structural Chemistry of Porphyrins), Moscow: Krasand, 2010.
8. Paolesse, R., Licoccia, S., Bandoli, G., Dolmella, A., and Boschi, T., *Inorg. Chem.*, 1994, vol. 33, no. 6, p. 1171.
9. Paolesse, R., Nardis, S., Sagone, F., and Khoury, R.G., *J. Org. Chem.*, 2001, vol. 66, no. 2, p. 550.
10. Ghosh, A. and Steene, E., *J. Inorg. Biochem.*, 2002, vol. 91, p. 423.
11. Steene, E., Wondimagegn, T., and Ghosh, A., *J. Phys. Chem. (B),* 2001, vol. 105, no. 46, p. 11406.
12. Paolesse, R., Licoccia, S., Fanciullo, M., Morgante, E., and Boschi, T., *Inorg. Chim. Acta*, 1993, vol. 203, p. 107.
13. Mandoj, F., Nardis, S., Pomarico, G., and Paolesse, R., *J. Porph. Phthaloc.*, 2008, vol. 12, p. 19.
14. *The Porphyrin Handbook,* Kadish, K.M., Smith, K.M., and Guilard, R., Eds., New York: Acad. Press, 2000, vol. 2, p. 235.
15. Cai, Sh., Licoccia, S., D'Ottavi, C., Paolesse, R., Nardis, S., Bulach, V., Zimmer, B., Shokhireva, T.Kh., and Walker, F.A., *Inorg. Chim. Acta*, 2002, p. 171.
16. Steene, E., Dey, A., and Ghosh, A., *J. Am. Chem. Soc.*, 2003, vol. 125, no. 52, p. 16300.
17. Karimov, D.R., *Candidate Sci. (Chem.) Dissertation*, Ivanovo, 2011.
18. Karmanova, T.V., Koifman, O.I., and Berezin, B.D., *Koord. Khim.*, 1983, vol. 9, no. 7, p. 919.
19. Berezin, B.D. and Koifman, O.I., *Russ. Chem. Rev.*, 1980, vol. 49, no. 12, p. 1188.
20. Simkhovich, L., Goldberg, I., and Gross, Z., *Inorg. Chem.*, 2002, vol. 41, no. 21, p. 5433.
21. Klyueva, M.E., *Doctoral (Chem.) Dissertation*, Ivanovo, 2006.
22. Samoletov, O.V., Bazanov, M.I., Evseev, A.A., Semeikin, A.S., Shatunov, P.A., and Andrievskii, G., *Izv. Vuzov, Ser. Khim. Khim. Tekhnol.*, 2006, vol. 49, no. 2, p. 87.
23. Tarasevich, M.R. and Radyushkina, K.A *Kataliz i elektrokataliz metalloporfirinami* (Catalysis and Metal Catalysis with Metal Porphyrins), Moscow: Nauka, 1982.
24. Liu, H.Ya., Chen, L., Yam, F., Zhan, H.Yi., Ying, X., Li Wang, X., Jiang, H.F., and Chang, C.K., *Chin. Chem. Lett.*, 2008, vol. 19, p. 1000.
25. Ngo, T.H., Van Rossom, W., Dehaen, W., and Maes, W., *Org. Biomol. Chem.*, 2009, vol. 7, p. 439.
26. Berezin, D.B., Shukhto, O.V., and Lazareva, N.V., *Russ. J. Inorg. Chem.*, 2012, vol. 57, no. 5, p. 744.
27. Karyakin, Yu.V. and Angelov, I.I., *Chistye khimicheskie veshchestva* (Pure Chemical Substances), Moscow: Khimiya, 1974.