CHEMICAL THERMODYNAMICS
AND THERMOCHEMISTRY

Thermal Stability of *meso*-Substituted Metal Corroles in Inert and Oxidative Media

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Abstract—The thermal stability of 5,10,15-triphenylcorrole as the simplest representative of *meso*-substituted corroles and its complexes with *d*-metals (Cu^{3+}, Mn^{3+}, Mn^{4+}, Co^{3+}, Co^{4+}, and Zn^{2+}) is studied for the first time via thermogravimetry in oxidizing and inert atmospheres. It is shown that corroles, both as free ligands and in the form of metal complexes, are less thermally stable than porphyrins with a similar structure. It is found that if the free ligands of porphyrins are thermally more stable with respect to thermal oxidation than *d*-metal complexes, the thermal stability of metal corroles can be both lower and higher than those of free ligands. It is concluded that the order of thermal stability of compounds MnCor < CoCor < H$_3$Cor < ZnCorH < CuCor is reversed upon moving from an oxidizing to an inert medium. It is shown that corroles complexes with many *d*-metals (Co, Mn, and others) readily participate in extracoordination reactions with electron-donating solvents, e.g., DMF, as is indicated by spectrophotometry and thermogravimetry.

INTRODUCTION

The metal complexes of aromatic macroheterocyclic compounds belonging to the class of corroles (H$_3$Cor) are of interest as components of new materials with unique optical, catalytic, chemoreceptor, and other properties [1]. The promise of these compounds is largely due to the stabilization of metals in the highest oxidation states by H$_3$Cor ligands, which is determined by the capability of the molecules of the complexes for reversible intramolecular electron transfer from metal atoms to the π-systems of the macrocycle. [2] This phenomenon, referred to as *non-innocence*, leads to the formation of π-radical forms of ligands in MCor complexes and can be controlled by changing the nature of the medium [3–6]. In particular, metal oxidation state 3+ in metal corroles of cobalt, manganese, and iron is stabilized in the presence of electron-donating molecules (B = DMF, Py), while the action of excess anions (Cl$^-$, AcO$^-$) favors the formation of stable state 4+ [2, 6, 7]. These forms of the compounds have easily distinguishable electronic absorption spectra (EAS, Fig. 1) [3, 6]:

$$(X^-)M^{4+}Cor^{-\cdot} + B \rightleftharpoons (B)M^{3+}Cor + X^-. \qquad (1)$$
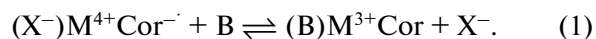
The behavior of the active components of new materials under polythermic conditions is one of their key physicochemical characteristics. In this work, we therefore investigated the thermal stability of 5,10,15-triphenylcorrole (I) complexes with transition metals
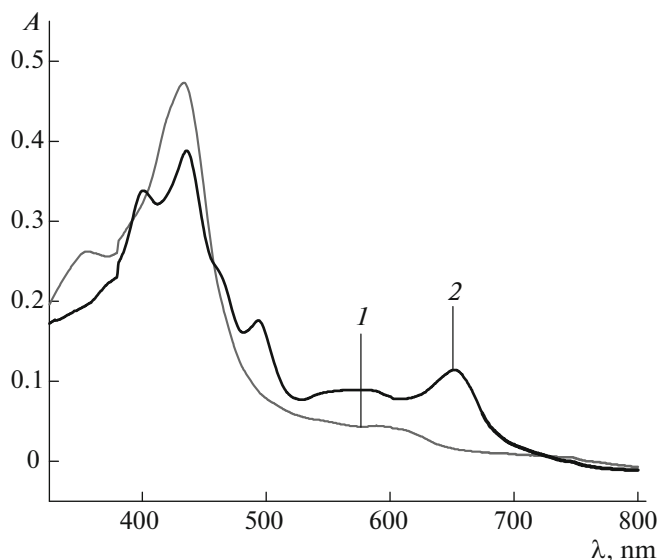
Fig. 1. Electronic absorption spectra of the complex of compound I with manganese (*1*) in CHCl$_3$ {(X$^-$)Mn^{4+}Cor} and (*2*) in DMF (Mn^{3+}Cor).

Parameters of the thermal destruction and thermal oxidation of 5,10,15-triphenylcorrole (I), 5,10,15,20-tetraphenylporphine (II) and their metal complexes.

Compound	Medium	Destruction of H-associate or extracomplex				Destruction of macrocycle							
		T_{st}, °C	T_{max}, °C	T_{fin}, °C	Δm, %	T_{st}, °C	T_{max}, °C	T_{fin}, °C	Δm, %	T_{st}, °C	T_{max}, °C	T_{fin}, °C	Δm, %
$H_2(ms\text{-}Ph)_4P$ (II)	$O_{2(air)}$ [14]	–	–	–		407	478	530					
	Ar	–	–	–		469.3	486.1	498.5	51.5				
$Co(ms\text{-}Ph)_4P$	$O_{2(air)}$ [14]					340	–	–					
	Ar					475.0	514.2	534.0	34.3	715.0	749.5	773.6	16.9
$Zn(ms\text{-}Ph)_4P$	$O_{2(air)}$ [14]					340	520	540					
	Ar					497.6	537.4	577.4	41.7				
$H_3(ms\text{-}Ph)_3Cor$ DMF (I)	Ar [13]	82.1	–	122.5	12.1	318	–	>900					
$H_3(ms\text{-}Ph)_3Cor$ (I)	$O_{2(air)}$	–	–	–	–	260	544	616	91.3				
$Mn^{III}(ms\text{-}Ph)_3Cor \cdot$ DMF	$O_{2(air)}$	115	128	142	7.0	235	347	420	82.3				
	Ar	108.3	146.1	196.8	13.2	361.4	430.0	518.7	20.6	811.6	–	>950	19.4
$(X)^{IV}Mn(ms\text{-}Ph)_3Cor$	Ar	154.1	175.7	207.5	5.9	354.4	431.6	546.7	28.7	826.0	–	>950	21.0
$Co^{III}(ms\text{-}Ph)_3Cor \cdot$ DMF	$O_{2(air)}$	51	100	139	11.8	253	413	530	74.9				
	Ar	107.1	144.5	184.5	16.5	304.0	363.4	464.8	18.9	723.7	755.0	801.3	9.6
$(X)Co^{IV}(ms\text{-}Ph)_3Cor$	Ar	167.6	212.4	246.1	9.2	320.4	396.3	466.7	18.3	585.7	–	626.9	8.4
										711.6	731.8	777.7	13.9
$Cu(ms\text{-}Ph)_3Cor$	$O_{2(air)}$	–	–	–		300	337	359	32.7				
						404	424	478	48.5				
	Ar	146.7	170.4	188.3	4.3	244.7	261.1	279.8	6.6	416.2	453.6	482.8	13.4
$DMF \cdot H^+[Zn(ms\text{-}Ph)_3Cor]^-$	$O_{2(air)}$	76	135	159	6.7	278	420	508	75.6				
	Ar	67.6	99.2	126.0	5.2	269.0	338.1	383.3	24.0	434.6	456.1	493.6	21.1

Δm is the mass loss; T_{st}, T_{max}, and T_{fin} are the temperatures of the start, maximum rate of the mass loss, and the end of decomposition stage, correspondingly.

Mn^{3+} and Mn^{4+}, Co^{3+} and Co^{4+}, and Cu^{3+} and Zn^{2+} under inert (Ar) and oxidative (air O_2) atmospheres via thermogravimetry. The thermal stabilities of corroles and porphyrins (H_2P, comp. II) of similar structure were compared, based on the concepts of the electronic structure and aromaticity of complexes.

EXPERIMENTAL

5,10,15-Triphenylcorrole (I) as a free ligand was synthesized according to the procedure described in [8]. Complexes of compounds I with d-metals (Mn^{3+}, Co^{3+}, Cu^{3+}, and Zn^{2+}) were prepared by reacting the corrole ligand (0.19×10^{-5} mol) with a tenfold molar excess of the corresponding metal (II) acetates in a medium of DMF (5–10 mL) [6, 9–11]. The temperature and reaction time were varied, depending on the nature of the metal: Mn, 150°C for 15 min; Co, 60°C for 1 h; Cu, 25°C upon mixing; Zn, for 60°C for 1.5 h. The reaction mixture was then diluted with water, and the reaction products were extracted with $CHCl_3$. The extracts were evaporated and the residue was chroma-

tographed on silica gel (eluent, chloroform). The zinc complex was destroyed on the column and therefore not subjected to chromatographic purification.

$Mn^{3+}Cor$ [λ (nm), (log ε), Py]: 407 (4.41) (sh); 440 (4.50); 505 (3.96); 552 (3.70) (br) 671 (3.69), ^1H NMR ($CDCl_3$): paramagnetic complex; region from −42.3 ppm (*meso*-phenyl protons) to +33.9 ppm (β-CH protons); MALDI FAB MS: $M^+ = 577.89$.

$Co^{3+}Cor$ [λ (nm), (log ε), Py]: 441 (4.36); 644 (3.94), ^1H NMR ($CDCl_3$): diamagnetic complex; region of 7.36–8.03 ppm.

$Cu^{3+}Cor$ [λ (nm), (log ε), Py]: 414 (4.91); 537 (3.76); 618 (3.46), ^1H NMR ($CDCl_3$): diamagnetic complex; region of 7.00–7.60 ppm.

$Zn^{2+}CorH$ [λ (nm), (log ε), Py]: 414 (4.37) (sh); 429 (4.43); 640 (4.01); 704 (3.95) (sh), ^1H NMR ($CDCl_3$): diamagnetic complex; region of 7.00–7.60 ppm (*meso*-phenyl and β-CH protons); + 0.09 (s, 1H, NH-proton).

Complex (X) $Co^{4+}Cor$ was formed upon dissolving the corresponding metal (3+) complex in chloroform,
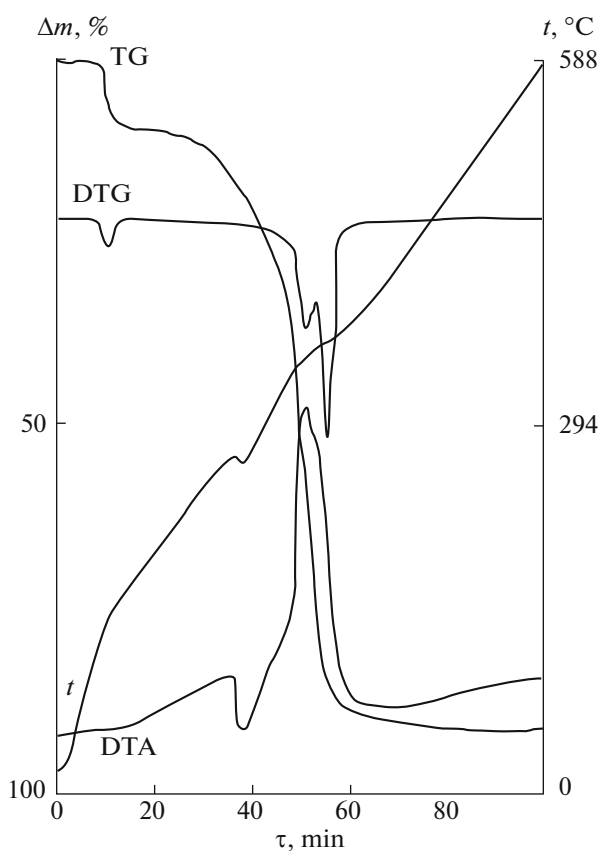
Fig. 2. Derivatogram of 5,10,15-triphenylcorrole (I) complex with manganese (3+) in an oxidative atmosphere (air).

followed by concentrating the solution and crystallization of the product. (X) $Mn^{4+}Cor$ was prepared in a similar fashion by stirring in $CHCl_3$ for 10 days or upon stirring 5% aqueous solution of HOAc and $Mn^{3+}Cor$ solution in dichloromethane for 15 min at room temperature, followed by neutralization of the acid and evaporation of the solvent:

(X)$Co^{4+}Cor$ [λ (nm), (log ε), $CHCl_3$]: 400 (4.27); 560 (3.74) (weak sh);

(X)$Mn^{4+}Cor$ [λ (nm), (log ε), $CHCl_3$]: 433 (4.57); 589 (3.54).

Thermal oxidative destruction of the compounds was studied using a 1000D derivatograph (Hungary), allowing us to record the change in the mass of a sample over time (TG), the rate of mass change (DTG), and the change in sample temperature during an experiment (the T curve), and to perform differential thermal analysis (the DTA curve) in atmospheric oxygen. Thermogravimetric measurements were performed in an argon atmosphere using a Netzsch TG 209 F1 derivatograph (Germany).

A weighed crystalline sample was placed into a platinum crucible and heated in a static atmosphere of Ar (3−7 mg) or O_2 (~15 mg) at a rate of 5−10 K/min in the temperature range of 298−1173 K (25−950°C). The samples were pre-dried to constant weight in a Fisher vacuum pistol at room temperature.

The electronic absorption spectra of the compounds were registered on a Shimadzu UV-1800 spectrophotometer, the ^{1}H NMR spectra were recorded on a Bruker spectrometer with an operating frequency of 500 MHz, and the mass spectra were obtained using a Shimadzu AXIMA Confidence MALDI-TOF mass spectrometer.

RESULTS AND DISCUSSION

Being π-electron−excess and less aromatic compounds than porphyrins [2, 12], corroles—both as free ligands and in the form of complexes—have lower chemical and thermal stability than H_2P with its similar structure [13]. Thus, 5,10,15-triphenylcorrole (I), compared to its closest porphyrin analog, 5,10,15,20-tetraphenylporphine (II), is less stable by almost 150°C with respect to thermal destruction in both oxidizing and inert atmospheres, according to the initial temperatures of macrocycle decomposition T_{st}^{O} = 260°C and T_{st}^{Ar} = 318°C (see table). Upon the crystallization of ligands I and II from an electron-donating solvent (DMF, Py), an additional low-temperature stage of the mass loss appears on the thermal curve of compound I at around 100°C, corresponding to the decomposition of H-associate $H_2CorH \cdot Solv$; this process does not occur with porphyrin II (table). The formation of H-associates of corroles with electron donors is due to the increased NH acidity of these macrocycles, compared to the *meso*-substituted H_2P [12, 13].

In the high-temperature region of the thermograms (235−530°C) of 5,10,15-triphenylcorrole (I) complexes (table, Fig. 2) obtained in an oxygen atmosphere, a loss of mass is observed that corresponds to macrocycle destruction to the carbon, nitrogen, and metals oxides and water. The total loss of mass during the thermal oxidation of macrocycles is quite high (Fig. 2). The stage of thermal oxidation is characterized by one *exo*-peak, as in the case of cobalt, manganese, and zinc complexes, or by two ($Cu^{3+}Cor$) *exo*-peaks on the DTA curve, the number of which could indicate that thermal destruction proceeds via different mechanisms [15]. Thermal oxidation in two steps is not typical for copper porphyrins [14]; with corroles complexes, we may assume that this corresponds to the destruction of two forms of the complex that are in equilibrium:

$$Cu^{3+}Cor \rightleftharpoons Cu^{2+}Cor^+. \qquad (2)$$

Like ligand I, metal corroles are less thermally stable than the corresponding complexes of compound II. However, if complexes in the case of porphyrin II are almost always less stable with respect to
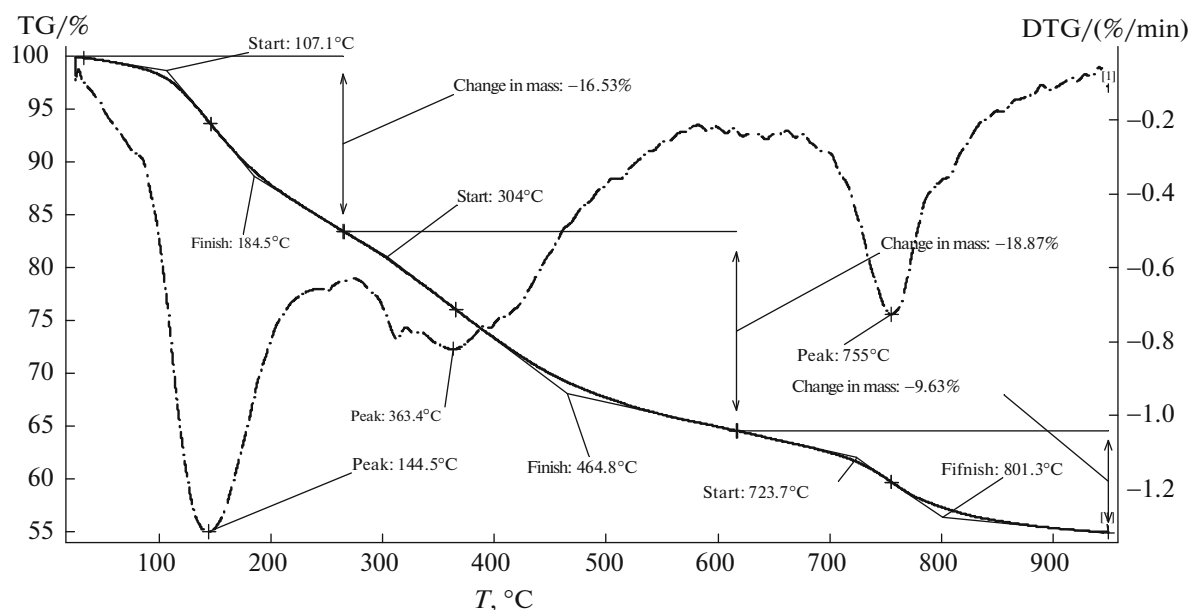
Fig. 3. Derivatogram of 5,10,15-triphenylcorrole (I) complex with cobalt (3+) in an inert atmosphere (argon).

oxidation under polytermic conditions than free ligands (table), metal corroles can be divided into two groups according to their stability with respect to thermal oxidation. The first group consists of cobalt (3+) and manganese (3+) complexes, which are prone to reversible changes in the oxidation state of the metal. On thermograms (Fig. 2) at temperatures of about 100°C, they exhibit a low-temperature stage of destruction corresponding to the elimination of solvent molecules (DMF) coordinated on their metal atoms, as is confirmed by the spectral data (Fig. 1); as for the stability of the macrocycles, they are less stable by 10−25°C than the ligand, according to the $T_{st.}$ values (table). The composition of Co^{3+}Cor and Mn^{3+}Cor extracomplexes, calculated from the losses of sample mass, approaches or is virtually identical to the stoichiometric ratio MCor : Solv = 1 : 1.

Complexes with Cu^{3+} and Zn^{2+}, for which an increase of the oxidation state of the metal is impossible, start to undergo thermal destruction at temperatures 20−40°C higher than those of the ligand. No pronounced low-temperature stages were detected for the copper complex, while the ZnCorH lost H-bonded molecules of DMF in the temperature range of 75−160°C. The initial temperatures of destruction (T_{st}) of metal corroles in an oxygen atmosphere thus differ slightly from the T_{st} of the ligand, compared to the MP. The thermal stability of these compounds is mainly determined by the sensitivity of the less aromatic macrocycle I to thermal oxidation, rather than by the nature of the metal.

To investigate thermal destruction in an inert medium, we prepared complexes of compound I with manganese and cobalt in the oxidation states of 3+

and 4+. A distinctive feature of the macrocycle destruction of metal corroles in an argon atmosphere is its multi-stage nature (two or three stages), along with a low total mass loss no greater than 50% (Fig. 3, table). In addition, a low-temperature stage of DMF elimination (Co^{3+}Cor, Mn^{3+}Cor, T_{st} = 107−108°C; ZnCorH, T_{st} = 68°C) or extraligands $Cl^−$, $AcO^−$ {(X)Co^{4+}Cor}, (X)Mn^{4+}Cor; Cu^{3+}Cor, T_{st} = 147−167°C) was observed for all studied forms of the complexes. For the copper complex with low extracoordination ability, the mass loss was low at the first stage. This is consistent with the concept of equilibrium $Cu^{2+} \leftrightarrow Cu^{3+}$ (2), which is difficult to shift upon the action of the medium [6, 7].

A comparison of the data on the destruction of metal corroles with metals in different states of oxidation in an inert atmosphere shows that the patterns of their thermal decomposition are close and differ only by the nature of the low-temperature stage. We may therefore conclude that the mechanism behind the destruction of non-extracoordinated complexes is of the same type under these conditions.

The initial temperatures of macrocycle destruction allow us to construct the corresponding order of the stability of the compounds in an inert atmosphere: Cu^{3+}Cor (244) < ZnCorH (269) CoCor (304−320) $\leqslant$ H_3Cor (318) < MnCor (354−361). In an oxidizing medium, Mn^{3+}Cor (235) < Co^{3+}Cor (253) < H_3Cor (260) < ZnCorH (278) < Cu^{3+}Cor (300). As can be seen, the order of the thermal stability of metal corroles is inversed upon a change in medium. The range of temperatures T_{st} is slightly higher in an inert medium than upon the thermal oxidation of the mol-

ecules. Maximum stabilization is observed for $Mn^{3+}Cor$ complex upon moving from an oxygen atmosphere to argon (126°C). The $Cu^{3+}Cor$ complex proved to be the most stable in a medium of O_2 and the least stable in an inert atmosphere. The presence of an oxidant in the system probably favors the formation of the highest oxidation state of the metal, from which it follows that Cu^{3+} state is more stable with respect to the action of atmospheric oxygen under polytermic conditions.

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