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Study of Thermal Stability of Tetraarenoporphyrazine Metal Complexes

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Abstract—Thermal stability in air of metal complexes of certain tetraarenoporphyrazines: tetrapyrazineporphyrazine, tetra-2,3-quinoxalinoporphyrazine, and tetra-2,3-naphtholocyanine, and also of copper complexes of tetra(*tert*-butyl)phthalocyanine, tetrapyrazineporphyrazine, and tetra-2,3-quinoxalinoporphyrazine substituted at the periphery was studied for the first time by the methods of thermogravimetry and differential thermal analysis. The effective thermal oxidation of these compounds occurs in the interval 620–820 K, and the tolerance for it is determined by both the metal nature and the structure of the macrocyclic ligand periphery.

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Structural modification of the phthalocyanine periphery is one of the major paths of the directional modification of properties of its metal complexes and of expansion of their application fields. Thus, revealing the interrelation of the structure of substituents at the periphery of macroheterocyclic ligands and the stability in various media, in particular, under thermal-oxidation conditions, becomes actual in connection with the prospect of application these compounds in air at high temperatures.

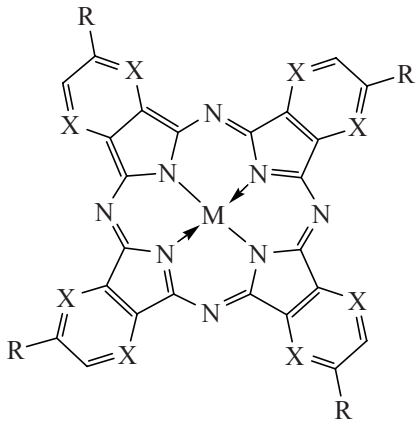
Comparative data on thermal-oxidative destruction of cobalt and iron complexes of some tetraphenylporphins and phthalocyanines have been published [1]. It is supposed [2] that the thermal oxidation of metal complexes of tetrapyrol macroheterocycles can be expressed by common Eq. (1):

$$ML + O_2 \rightarrow M_xO_y + \text{thermal oxidation products.} \quad (1)$$

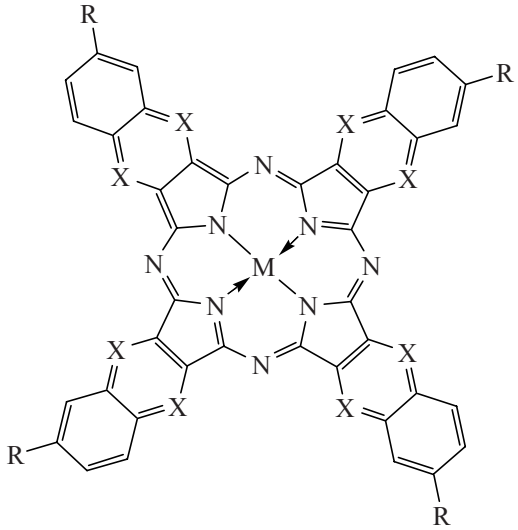
The run of the DTA and TG curves of these two groups of complexes points to a complicated character of the thermal destruction process involving parallel occurring of several reactions, including detachment of substituents, demetallization, destruction of a macroring, and secondary oxidation of reaction products. A distinctive feature of the thermal destruction of metal porphyrins is the presence of two well pronounced exoeffects, which are not observed in the case of phthalocyanines. At the same time, in spite of certain stabilization of a macroring by electron-donor substituents and destabilization by electron-acceptor groups at the periphery of the porphyrin macrocycle, the studied compounds have similar thermal stability, and the macroring nature does not exert a dominant influence on this parameter.

Probably this is the reason why the study of the thermal stability of tetraazoporphin compounds, which mainly belong to metal phthalocyanines [2–6], consider not the effect of structural factors, but the nature of complex-forming metals. The aim of the present work was to study the thermal behavior in air of tetrapyrazineporphyrazine (PzcM), tetra-2,3-naphtholocyanine (2,3-NcM), and tetra-2,3-quinoxalinoporphyrazine (2,3-QxcM) metal complexes for revealing the influence of the structure of substituents at the ligand periphery (structural phthalocyanine modification) on the thermal stability of metal tetraazoporphins, that is of both theoretical and practical interest.

Typical derivatograms of the studied metal complexes presented in Figs. 1 and 2 are characterized by a weight loss due to removal of water of crystallization at temperatures 37–423 K, after which the weight of samples remains practically constant up to the beginning of the thermal destruction, as demonstrated by a sharp weight loss and a strong exothermal effect,



X = CH (PcM), X = N (PzcM)



X = CH (NcM), X = N (QcxM)

R = H, *t*-Bu

which is also characteristic for the thermal oxidation of phthalocyanine metal complex [1, 2, 5, 6]. The complicated run of the DTA curves characterized by the presence of resolved and partially resolved maxima, and also of steps of TG curve slopes point to a parallel occurring of several processes superimposing on one another and including, apparently, demetallization, destruction of a macroring, and oxidation of the destruction products.

Thermal stability of complex compounds can be estimated using various parameters of derivatograms. In our opinion the most important and informative are temperatures of the decomposition beginning (T_{db}) and of the maximal exothermal effect (T_{ee}). The first temperature limits from above the temperature exploitation field and thus has a practical value, and the second corresponds to the most intensive destruction of the molecule macroring and can serve as a thermodynamic characteristic of a metal complex stability toward thermal oxidation.

These characteristic temperatures for the studied compounds are given in the table in comparison with

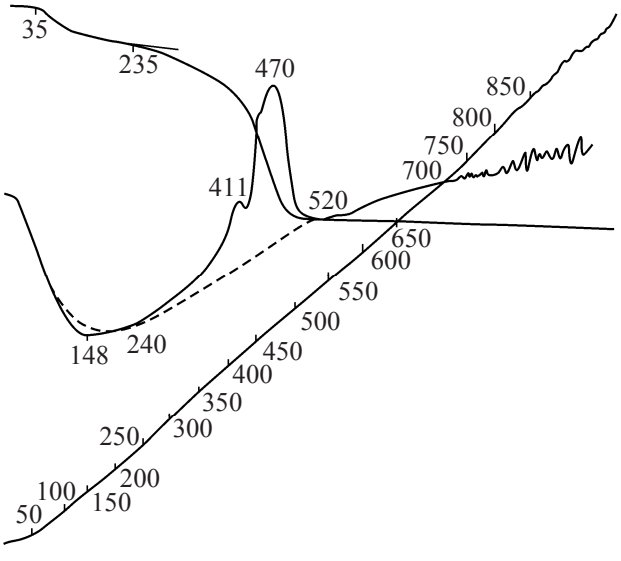


Fig. 1. Derivatogram of copper(II) complex with tetrapyrazineporphyrazine (PzcCu).

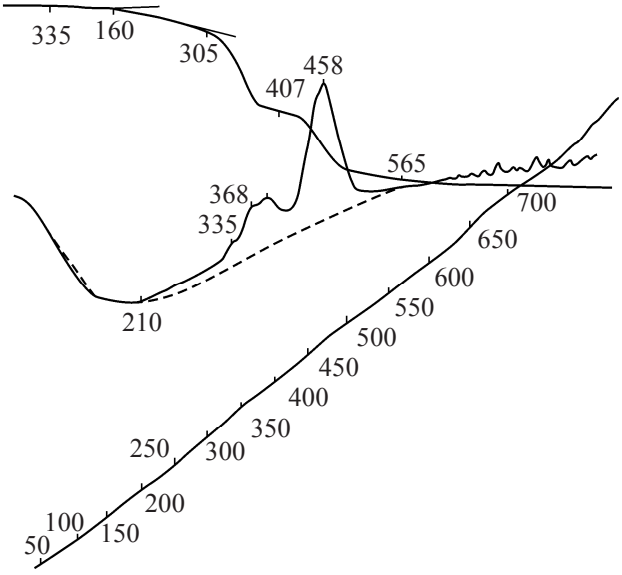


Fig. 2. Derivatogram of copper(II) complex with tetra(*tert*-butyl)tetra-2,3-quinoxalinoporphyrazine [Qxc(*t*-Bu)$_4$Cu].

Temperatures of the decomposing beginning and of the maximal exothermal effect for thermal oxidation of metal complexes of tetraarenoporphyrazines

Compound	T_{db}, K	T_{ee}, K	Compound	T_{db}, K	T_{ee}, K
PcCu	660	699	PzcCu	684	743
Pc(*t*-Bu)$_4$Cu	617	633	Pzc(*t*-Bu)$_4$Cu	623	725
PcCo	673 [5]	718 [5]	PzcNi	682	704
PcMg	643 [5]	693 [5]	PzcMn	655	707
PcFe	593 [1]	623 [1]	PzcCrCl	648	668, 741
$PcSnCl_2$	713 [5]	773 [5]			
2,3-NcCu	669	661, 754	2,3-QxcCu	676	693, 725
2,3-NcCo	653	687, 741	2,3-Qxc(*t*-Bu)$_4$Cu	658	731
2,3-NcNi	673	688, 802	2,3-QxcCo	693	712, 731
2,3-NcZn	656	748	2,3-QxcMn	659	749
2,3-NcMg	648	711	2,3-QxcGaCl	643	730, 773
2,3-NcMn	699	812, 877	2,3-QxcCrCl	612	637, 695

the characteristics of phthalocyanine complexes of the same metals.

The fact that the presence of two well pronounced exothermal effects is characteristic only for the complexes 2,3-NcM and 2,3-QxcM among all studied metal tetraarenoporphyrazines, as well as for metalloporphyrins, attracts our attention. The reasons of this pheno-menon are not clear as yet, but its correlation with increasing size of ligands is undoubtful.

It is convenient to judge the effects of the metal nature and ligand structure on the thermal stability of the complexes by T_{db} and T_{ee} variation in the isoligand [Eqs. (2)–(5) and (11)–(14)] and isometal [Eqs. (6)–(10) and (15)–(19)] series, respectively.

$$\text{PcM: } SnCl_2 > {}^{\Delta 40}\text{Co} > {}^{\Delta 13}\text{Cu} > {}^{\Delta 17}\text{Mg} > {}^{\Delta 50}\text{Fe}, \quad (2)$$

$$\text{2,3-NcM: Mn} > {}^{\Delta 26}\text{Ni} > {}^{\Delta 4}\text{Cu} > {}^{\Delta 16}\text{Co} \approx \text{Zn} > {}^{\Delta 6}\text{Mg}, \quad (3)$$

$$\text{PzcM: Cu} \approx \text{Ni} > {}^{\Delta 27}\text{Mn} > {}^{\Delta 7}\text{CrCl}, \quad (4)$$

$$\text{2,3-QxcM: Co} > {}^{\Delta 17}\text{Cu} > {}^{\Delta 17}\text{Mn} > {}^{\Delta 16}\text{GaCl} > {}^{\Delta 31}\text{CrCl}, \quad (5)$$

$$\text{Cu(II) Pzc} > {}^{\Delta 8}\text{2,3-Qxc} > {}^{\Delta 7}\text{2,3-Nc} > {}^{\Delta 9}\text{Pc} \approx \text{2,3-Qxc}(t\text{-Bu})_4 > {}^{\Delta 35}\text{Pzc}(t\text{-Bu})_4 > {}^{\Delta 6}\text{Pc}(t\text{-Bu})_4, \quad (6)$$

$$\text{Co(II) 2,3-Qxc} > {}^{\Delta 20}\text{Pc} > {}^{\Delta 20}\text{2,3-Nc}, \quad (7)$$

$$\text{Mn(II) 2,3-Nc} > {}^{\Delta 40}\text{2,3-Qxc} > {}^{\Delta 4}\text{Pzc}, \quad (8)$$

$$\text{CrCl Pzc} > {}^{\Delta 36}\text{2,3-Qxc}, \quad (9)$$

$$\text{Mg 2,3-Nc} > {}^{\Delta 5}\text{Pc}. \quad (10)$$

An examination of the T_{db} data does not allow us to reveal any regularities and correlations between ligand structures, metal natures, and thermal properties of metal tetraarenoporphyrazines. It suggests that the beginning of complexes decomposition is determined by a number of random or not considered factors depending not only on the properties, but also on the previous history of samples, for example, the crystalline modification of the substance, the ratio of amorphous and crystalline phases, the size of crystals and the amorphous phase morphology, the presence, nature, and composition of crystal solvates and hydrates, etc., and even on the presence of impurities. Though substances can be standardized (reduced to an equal "standard" state) with respect to some of these parameters, it is in essence impossible with respect to other parameters.

$$\text{PcM: } SnCl_2 > {}^{\Delta 55}\text{Co} > {}^{\Delta 19}\text{Cu} > {}^{\Delta 6}\text{Mg} > {}^{\Delta 70}\text{Fe}, \quad (11)$$

$$\text{2,3-NcM: Mn} > {}^{\Delta 64}\text{Zn} > {}^{\Delta 37}\text{Mg} > {}^{\Delta 23}\text{Ni} \approx \text{Co} > {}^{\Delta 26}\text{Cu}, \quad (12)$$

$$\text{PzcM: Cu} > {}^{\Delta 34}\text{Mn} > {}^{\Delta 3}\text{Ni} > {}^{\Delta 36}\text{CrCl}, \quad (13)$$

$$\text{2,3-QxcM: Mn} > {}^{\Delta 19}\text{GaCl} > {}^{\Delta 18}\text{Co} > {}^{\Delta 19}\text{Cu} > {}^{\Delta 56}\text{CrCl}, \quad (14)$$

$$\text{Cu(II) Pzc} > {}^{\Delta 12}\text{2,3-Qxc}(t\text{-Bu})_4 > {}^{\Delta 6}\text{Pzc}(t\text{-Bu})_4 > {}^{\Delta 26}\text{Pc} > {}^{\Delta 6}\text{2,3-Qxc} > {}^{\Delta 32}\text{2,3-Nc} > {}^{\Delta 28}\text{Pc}(t\text{-Bu})_4, \quad (15)$$

$$\text{Co(II) Pc} > {}^{\Delta 6}\text{2,3-Qxc} > {}^{\Delta 25}\text{2,3Nc}, \quad (16)$$

$$\text{Mn(II) 2,3-Nc} > {}^{\Delta 63}\text{2,3-Qxc} > {}^{\Delta 42}\text{Pzc}, \quad (17)$$

$$\text{CrCl Pzc} > {}^{\Delta 31}\text{2,3-Qxc}, \quad (18)$$

$$\text{Mg 2,3-Nc} > {}^{\Delta 18}\text{Pc}. \quad (19)$$

On the contrary, the examination of T_{ee} variation apparently connected with the intrinsic thermal oxidation of the main substance in isoligand and isometal series allows us to reveal some regularities.

First of all, it is necessary to note that T_{ee} of the cobalt complexes in the PcM, 2,3-NcM and 2,3-QxcM series are higher by approximately 20° than those of the copper complexes. It is important that the sequence

of ligands in isometal Cu(II) and Co(II) series is retained, and passing from one ligand to another is accompanied by approximately equal T_{ee} variations for the both metals.

On passing from Cu(II) to Mn(II) or to Mg the arrangement of ligands in isometal series is changed, whereas on passing from Cu(II) to CrCl it remains the same.

Judging from temperatures of the decomposition beginning, the injection of *tert*-butyl groups at the periphery of a ligand molecule, i.e. passing from unreplaced complexes of tetraarenoporphyrazines to their *tert*-butyl substituted unambiguously results in a thermal stability decrease. However T_{ee} variations do not confirm this conclusion, and the example of copper complexes shows that such a ligand variation can both increase (in the case of 2,3-QxcM) and reduce (in the case of PzcM and especially PcM) the stability toward thermal oxidation.

The hypothesis on the thermal stability increase owing to the protection of a central atom of metal tetraarenoporphyrazines by extra-ligands (EL) (due to screening the metal and the necessity of the initial rapture of M–EL bonds), as compared to complexes of divalent metals, is not confirmed by our data, at least, for trivalent metals.

The nature of a ligand strongly affects the thermal-oxidative destruction. The variation of the ligand nature changes the thermal stability of the copper complexes within the limits of 110° in terms of T_{ee}.

The contribution of the metal nature is no less important, and the thermal stability of the complexes varies in the isoligand series within the range of 125–150°.

The examination of results obtained shows that the stability of the metal complexes of tetraarenoporphyrazines is not determined exclusively by the metal or ligand nature, but depends on several factors, most essential of which are: the nature of the metal-macrocyclic ligand bond, the ability of a central ion to increase its oxidation state, the electron density on a macrocycle, and also the extent of distortion of the molecular planar structure. The combination of these factors results in the appearance of an ambiguous pattern and in the absence of a correlation between thermal stability and each of these factors separately.

EXPERIMENTAL

Metal complexes of tetraarenoporphyrazines were obtained by the nitrile procedure: PzcM from 2,3-pyrazinecarbonitrile [7], 2,3-NcM from 2,3-naphthalenecarbonitrile [8], 2,3-QxcM from 2,3-quinoxalinecarbonitrile [7], Pc $(t\text{-Bu})_4$M from 4-*tert*-butylphthalo-nitrile [9], Pzc$(t\text{-Bu})_4$M from 5-*tert*-butyl-2,3-pyrazinedicarbonitrile [10], and 2,3-Qxc$(t\text{-Bu})_4$M from 6-*tert*-butyl-2,3-quinoxalinecarbonitrile [11]. They were purified by traditional methods and identified by spectral characteristics [12] and elemental analysis data. Before using samples were dried up to a constant weight in a vacuum drying box at 353 K and residual pressure of 10 kPa, and carefully ground.

The thermal stability of the metal complexes of tetraarenoporphyrazines was studied by the thermogravimetric method on a MOM-1000D (Hungary) derivatograph at a heating rate of 5 deg min^{-1}; stability of TG signals was 50 mg, DTG = 1 mV, DTA = 250 μV, T = 1000°C per 250 mm of a scale.

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