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# Stability of Nonplanar *N*-Methylporphyrins and Their Zinc Complexes

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**Abstract**—Resistance of *N*-methyl-substituted porphyrins and their Zn(II) complexes to thermooxidative degradation and to the action of a DMSO–AcOH proton-donor solvent was studied by thermogravimetry and chemical kinetics. The fairly low stability of the complexes is caused by decreased planarity and, as a consequence, aromaticity of the macrorings and also by the tendency of the complexes to demethylation. The stability of the zinc complexes in AcOH varies in parallel with the degree of nonplanarity and resistance to thermooxidative degradation of their ligands.

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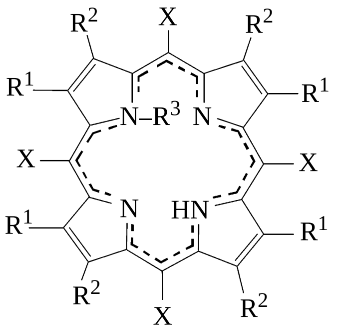
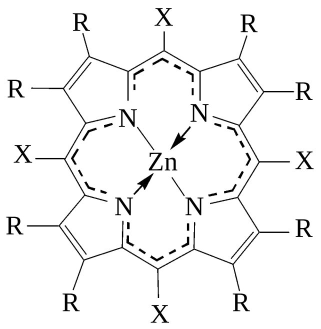
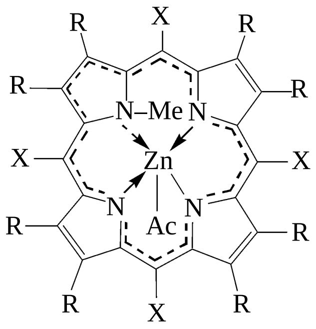
Porphyrins ($H_2P$), such as compounds **I**–**V**, are most commonly applied in engineering, technology, and medicine in the form of metal complexes **VI**–**IX**, many of which are used for constructing supramolecular nanostructures, are perspective catalysts and photosensitizers, pigments, and materials for nonlinear optics [1]. Therefore, to assess resistance porphyrin metal complexes (MP) to various external factors (thermal, photochemical, and chemical reagents and solvents) is an important criterion of their applicability.



**I–V**



**VI, VII**



**VIII, IX**

$R^1$ = Me, $R^2$ = Bu, $R^3$ = X = H (**I**); $R^1$ = $R^2$ = Et, $R^3$ = X = H (**II**); $R^1$ = $R^2$ = $R^3$ = H, X = Ph (**III**); $R^1$ = $R^2$ = Et, $R^3$ = Me, X = H (**IV**); $R^1$ = $R^2$ = H, $R^3$ = Me, X = Ph (**V**); R = Et, X = H (**VI**); R = H, X = Ph (**IX**).

Porphyrin-like molecules are divided into porphyrins and their analogs [2]. N-Substituted porphyrins, for example, monosubstituted compounds H(NR)P **IV** and **V** can only arbitrarily be placed into the first group. Characteristic features of $H_2P$ are the presence of an $N_4H_2$ reaction center and the porphin-like structure of the main π-conjugation contour [3]. Replacement of the hydrogen atom of one endocyclic NH group in $H_2P$ by a hydrocarbon fragment, such as methyl, changes the structure of the reaction center of the ligands from $N_2(NH)_2$ (compounds **I**–**III**) to $N_2$(NH)(NR) (compounds **IV** and **V**) and of complexes with divalent metal ions, from $MN_4$ (compounds **VI** and **VII**) to (X)$MN_3$(NMe) (compounds **VIII and IX**), where **X** is covalently bound counterion. The conjugated porphyrin π system in *N*-methyl-substituted ligands H(NMe)P is preserved (compounds **I**–**V**), but it changes strongly in going to N-substituted complexes (X)M(NMe)P [4, 5] (compounds **VI**–**IX**).

N-Substitution in $H_2P$ much redistributes the electron density in the parent molecule both due to electronic effects of the additional functional group ($R^3$) and due to disturbance of the planar macroring structure with the N-substituted fragment drawn strongly out of the plain. The degree of nonplanarity of the molecule depends on the size of the N-substituent and on the rigidity (aromaticity) of the starting unsubstituted porphyrin [4].

Such changes in molecular structure essentially affect resistance of N-substituted ligands and their complexes to various physical factors and chemical reagents. Thus it is known that complexes with N-substituted ligands are unstable, and even the most stable of them undergo dissociation [Eq. (1)] even at pH > 3 [4].

$$(AcO)Zn(NMe)P + AcOH \longrightarrow H(NMe)P + Zn(OAc)_2. \quad (1)$$

In the medium of organic bases (amines), complexes of N-substituted porphyrins enter nucleophilic substitution reactions [Eq. (2)] and lose the N-substituent, whereas their ligands are more stable in dealkylation (dearylation) reactions [6]. Quantitative data on the resistance of these compounds to various factors are absent from the literature, and the mechanisms of their dissociation (degradation) are also unknown.

$$(X)M(NR)P + RNH_2 \longrightarrow MP + [R_2NH_2]^+X^-. \quad (2)$$

The promise N-substituted porphyrins capable of stabilizing unusual oxidation states of metal ions [Fe(II), Co(II), etc.] hold in catalysis [4] makes it urgent to study their behavior in aggressive media and in polythermal conditions. To reveal reasons for the low stability of N-substituted porphyrins and their complexes and to establish certain regularities of the stability decrease, we studied resistance of zinc(II) complexes **VIII** and **IX** with N-substituted ligands, specifically *N*-methyloctaethylporphine (**IV**) and *N*-methyltetraphenylporphine (**V**), to thermooxidative degradation in the solid phase and to dissociation in solutions containing a proton-donor component, as well as resistance of ligands **IV** and **V** to thermooxidation. The study was carried out by thermogravimetry and chemical kinetics.

Table 1 presents the results of studying thermooxidative degradation of compounds **IV**, **V**, **VIII**, and **IX** together with published data [7] for their structural analogs, tetraphenylporphine (**III**), its complex with Zn(II) (**VII**), and 2,3,6,7-tetrabutyl-1,4,5,8-tetramethylporphine (**I**) as a model β-octaalkyl-substituted compound. The thermoanalytical curves for thermooxidative degradation of N-substituted compounds **IV** and **VIII** are given in Fig. 1. The kinetic parameters of reaction (1) involving zinc complexes of N-substituted porphyrins **VIII** and **IX** in the DMSO–AcOH medium are shown in Table 2. The concentration dependences of the apparent rate constants of reaction (1) are presented in Fig. 2.

**Table 1.** Thermooxidative degradation of porphyrins **I** and **III**–**V** and their zinc(II) complexes **VII**–**IX**[a]

| Comp. no. | $T_b$, °C | $T_m$, °C | $T_t$, °C | $\Delta_t$, % | $\Delta_e$, % |
|---|---|---|---|---|---|
| **I**[b] | 400 | 530 | 620 | – | – |
| **III**[b] | 407 | 478 | 530 | – | – |
| **IV** | 310 | 478 | 600 | – | – |
| **V** | 260 | 625 | 682 | – | – |
| **VII**[b] | 340 | 520 | 540 | – | – |
| **VIII** | 212 | 534 | 592 | 12.11 | 11.92 |
| **IX** | 230 | 476 | 598 | 10.82 | 10.5 |

[a] Processes studied: $H_2P \rightarrow$ N, C, and H oxides and MPC $\rightarrow$ ZnO + N, C, and H oxides. $T_b$ is the initial process temperature; $T_m$, temperature of the maximal exo effect; $T_t$, final process temperature; and $\Delta_t$ and $\Delta_t$, theoretical and experimental weights of ZnO. [b] Data of [7].

**Table 2.** Kinetic parameters of reaction (1) of dissociation of zinc(II) *N*-methylporphyrin complexes **VIII** and **IX** and zinc tetraphenylporphine (**VII**) in DMSO–AcOH ($c_{MP}$ $6.7 \times 10^{-5}$ M, 298 K)

| $c_{AcOH}$, M | $k_{app} \times 10^3$, $s^{-1}$ | $E_a$, $kJ\,mol^{-1}$ | $\Delta S^{\neq}$ $J\,mol^{-1}\,K^{-1}$ |
|---|---|---|---|
| Compound **VII**[a] | | | |
| 17.5 | 0.26 ± 0.02 | 46.1 ± 2.0 | –155 ± 8 |
| Compound **VIII** | | | |
| 17.5 | 1.87 ± 0.09 | 85.8 ± 7.4 | –13 ± 4 |
| 16.2 | 0.97 ± 0.06 | 102.8 ± 7.6 | 40 ± 16 |
| 12.8 | 0.11 ± 0.01 | 92.5 ± 17.7 | –18 ± 7 |
| Compound **IX** | | | |
| 17.5 | 26.65 ± 2.03 | 27.9 ± 6.3 | –189 ± 30 |
| 16.2 | 34.18 ± 0.32 | 47.8 ± 11.2 | –120 ± 35 |
| 14.1 | 47.36 ± 3.72 | 66.0 ± 15.1 | –57 ± 10 |
| 10.9 | 30.88 ± 3.11 | 72.8 ± 14.3 | –38 ± 9 |
| 9.43 | 9.19 ± 0.97 | 38.4 ± 7.0 | –163 ± 24 |

[a] Data of [3].

One more goal of the present work was to correlate the degree of nonplanarity of metal porphyrins or their ligands and resistance of the complexes to dissociation in acid medium and to thermooxidative degradation.

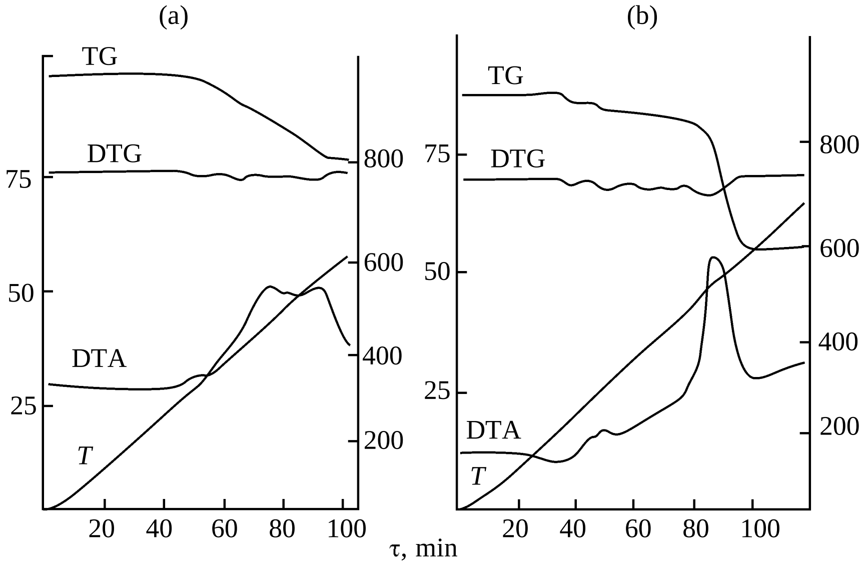


**Fig. 1.** Thermoanalytical curves of (a) *N*-methyloctaethylporphine (**IV**) and (b) its zinc complex (**VIII**).

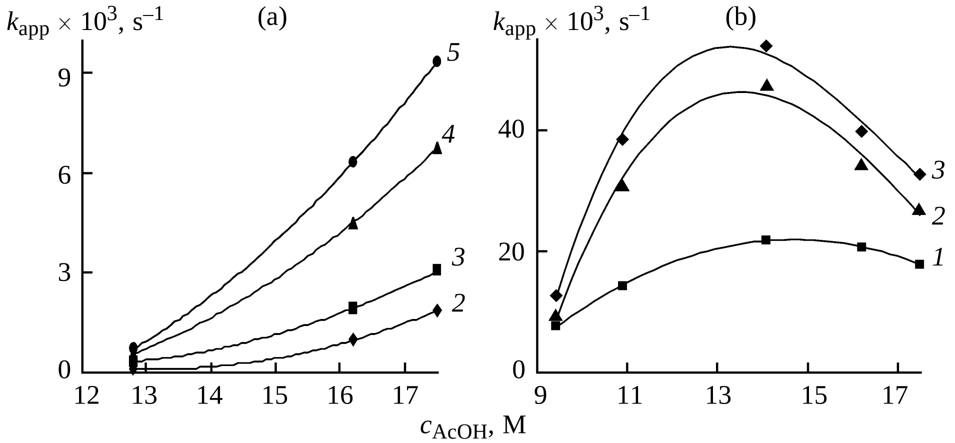


**Fig. 2.** Dependences of apparent dissociation rate constants ($k_{app}$) of complexes (a) **VIII** and (b) **IX** on AcOH concentration in DMSO. *T*, K: (*1*) 293, (*2*) 298, (*3*) 303, (*4*) 308, and (*5*) 313.

According to the general regularities of thermo-oxidative degradation of porphyrins and their complexes, established in [7], the process is characterized by several stages including oxidation and macroring opening, burning, and complete weight loss due to the formation of gaseous nitrogen, carbon, and hydrogen oxides (Table 1 and Fig. 1).

As compared to classical MP [7], the degradation scheme of N-substituted metal porphyrins **VIII** and **IX** have certain specific features. The thermooxidative degradation of Zn(II) complexes of *N*-methyloctaethylporphine (**VIII**) and *N*-methyltetraphenylporphin (**IX**) begins with two consecutive stages accompanied by a loss of weight (Δ, %) and small exothermic peaks on the DTA curve (Fig. 1). Within the experimental error, the weight loss in the first stage numerically corresponds to the weight loss due to cleavage and removal of $CH_3$ group from the sample [theoretical ($\Delta_t$) and experimental ($\Delta_e$) values fit each other and equal 7.85, 8.78 and 7.6, 8.9% for complexes **VIII** and **IX**, respectively]. The weight loss in the second stage results from removal of the axial acido ligand AcO- ($\Delta_t$ and $\Delta_e$ are 2.0, 2.4 and 2.1, 2.31% for compounds **VIII** and **IX**, respectively). Thus, the degradation of the zinc porphyrins studied begins with cleavage of the *N*-methyl group from the macroring and oxidation of this group by air oxygen, which is favored by the more pronounced out-of-plane location of this group in complexes as compared with starting ligands [4] and also by the unstable hybrid state of the substituted nitrogen atom [5, 8], leading to a strained conformation of compounds **VIII** and **IX**. The *d* metal in the N-substituted molecule catalyzes cleavage of the N-substituent both in solution [6] and in solid. The subsequent intramolecular rearrangement in thermally demethylated compounds results in formation of practically planar complexes of Zn octaethylporphine (**VI**) and Zn tetraphenylporphine (**VII**). In the second stage of the process, the acetate residue is removed from the complex immediately after methyl removal (Fig. 1). Thus, the chemical transformations that initiate thermooxidation of complexes with N-substituted porphyrins can schematically presented by the overall reaction scheme (3).

$$\mathrm{(AcO)Zn(NMe)P} + 1/2\mathrm{O_2} \longrightarrow \mathrm{ZnP} + \mathrm{CH_2O} + \mathrm{AcOH}. \quad (3)$$

Oxidation and degradation of the chromophore molecule begin immediately after the oxidized N-substituent and the axial ligand have been removed, and these processes are characterized by exothermic peaks in the DTA curve (Fig. 1), the number of peaks varying from one to two depending on the nature of the porphyrin ligand. It is necessary to note that under these conditions MP bearing no endocyclic substituents, such as compound **VII**, do not undergo thermooxidation (Table 1). Apparently, the subsequent oxidation of N-substituted complexes (AcO)Zn(NMe)P is connected with the fact that the demethylated nitrogen atom has no time to form the stable $sp^2$ state.

Oxidation of Zn(II) metal porphyrins is completed by formation of zinc(II) oxide. As seen from Table 1, the experimental and calculated weights of the ZnO formed nicely fit each other within the experimental error, which confirms the composition of the complexes once more.

Comparison of the thermooxidation data for compounds **VII** and **IX** (Table 1) shows that methylation of the central nitrogen atom essentially (by 110°C) decreases the initial degradation temperature ($T_\mathrm{i}$) of the porphyrin complexes. Compound **VIII** containing ligand **IV** that is less inclined to deformations than ligand **V** loses the N-substituent easier than complex **IX**, since this process is accompanied by transition of the molecule from the strained nonplanar conformation into a planar one.

The thermal stability series for porphyrin ligands **III** > **IV** > **V** somewhat differs from the corresponding series for the complexes **VII** > **IX** > **VIII**. Furthermore, compounds **IV** and **V** are thermally more stable than compounds **VIII** and **IX** and undergo oxidative degradation without preliminary cleavage of the $CH_3$ group (Fig. 1). The lower resistance of MP to thermooxidative degradation results from the presence of active oxidation, viz. metal atoms, in the complexes. In the case of nonplanar MP, the steric structure of the ligand makes metal free valences difficult to saturate, thus ensuring an appreciable effective charge on this atom. Furthermore, the tendency of N-methylated complexes to demethylation reactions (2) at elevated temperatures, too, makes them less stable thermally.

Methylation of the NH group of the $N_4H_2$ reaction center essentially (by 90 and 147°C, respectively) decreases the initial thermooxidation temperature of the *N*-methyloctaethylporphine (**IV**) and *N*-methyltetraphenylporphine (**V**) ligands compared to their unsubstituted analogs **I** and **III** (Table 1) [7]. This is obviously connected with the less effective conjugation in and decreased aromaticity of nonplanar macrorings. The most distorted ligand **V** is least resistant to to thermooxidative degradation. Earlier we showed, by fluorescence spectroscopy and molecular mechanics [9], that compound **IV** is less planar than unsubstituted compound **II** but much more planar than ligand **V**. By resistance to thermooxidative degradation the compounds studied can be arranged in the analogous series **I** ≈ **III** > **IV** > **V**.

To assess the effect of the nonplanar structure of metal porphyrins on their resistance to protondonor reagents, we studied the dissociation kinetics of zinc(II) complexes with N-substituted compounds **VIII** and **IX** in the DMSO–AcOH medium and in glacial AcOH.

It was shown that the complexes with nonplanar ligands are less resistant or dissociation in an ionizing medium than analogous complexes of tetraphenylporphine (**VII**) and other planar classical $H_2P$ [3]. This suggests a negative effect of the nonplanar structure of the macroring and factors favoring distortion on the stability of its complex compounds. Thus, the apparent dissociation rate constant of complex **IX** in glacial acetic acid at 298 K (Table 2) is higher by a factor of 15 than that of compound **VIII** and by two orders of magnitude than that of unsubstituted complex **VII**.

Thus, the kinetic stability of the complexes in glacial AcOH decreases with increasing conformational mobility of their ligands [4, 9] and follows the series **VII** > **VIII** > **IX**. This series parallels the series of resistance of the corresponding ligands to thermooxidative degradation (Table 1).

The dissociation of the metal porphyrins in the DMSO–AcOH medium is described by two types of dependences of the apparent rate constants of reaction (1) ($k_{\mathrm{app}}^{298}$) on AcOH concentration ($c_{\mathrm{AcOH}}$) (Fig. 2, Table 2). The dissociation rate of compound **VIII** steadily decreases with decreasing AcOH concentration in DMSO (Fig. 2a), whereas the $k_{\mathrm{app}} = f(c_{\mathrm{AcOH}})$ dependence for the less stable complex **IX** is more complicated and has a maximum in the region of ~14 M AcOH (Fig. 2b). Dependences of the latter type have never been observed for dissociation of metal porphyrins.

The presence of different $k_{\mathrm{app}} = f(c_{\mathrm{AcOH}})$ dependences points to different mechanisms of reaction (1) for these MP, involving different attacking particles. A diversity of attacking particles ($\mathrm{DMSO \cdot H^+}$, $\mathrm{AcOH \cdot H^+}$, AcOH, etc.) is possible in DMSO–AcOH, but the absence of data on their equilibrium concentrations does not allow us to write complete kinetic equations and to calculate true rate constants of reaction (1) in this medium. The complication of the concentration dependence can be caused by a change of the attacking particle on the change of solvent composition or by simultaneous participation of several particles.

According to [10], complexes like $\mathrm{(X)Zn(NMe) \cdot TPP}$ in the MeOH–HCl system dissociate under the action of one proton (participates in the limiting stage), as opposed to two protons in the case of metal porphyrins without endocyclic substituents. It was shown in [10] that the reaction rate does not depend on water additions up to the concentration of 0.2 M, but it is sensitive to the presence of salt background (NaCl and $\mathrm{[(Et)_4N]Cl}$) in the system. In the latter case, the reaction rate increases by 20%. We can suggest that the dissociation mechanism of complexes (X)M(NMe)TPP in the MeOH–HCl medium is acido-protolytic in part, i.e. the complex dissociates under the action of an undissociated acid molecule. Earlier the acido-protolytic mechanism was suggested and justified for the dissociation of Mg(II) azoporphine complexes [Eq. (4)] in $\mathrm{C_6H_6}$–AcOH and EtOH–AcOH [11, 12]. One of the necessary conditions for this mechanism operate is the presence of a high effective positive charge on the metal atom and of an effective negative charge on any nucleophilic center in MP.

$$\mathrm{MP} \overset{\mathrm{HX}}{\rightleftarrows} \mathrm{(X)MPH^+} \xrightarrow{\mathrm{HX}} \mathrm{H_2P + MX_2}. \qquad (4)$$

The fact that Zn(II) complexes with N-substituted porphyrins partially meet the above conditions may promote (in a certain ionizing medium) their acido-protolytic dissociation. However, it is improbable that the acidoprotolytic mechanism of reaction (1) is realized in the medium of an electron-donor solvent, such as AcOH. However, it is not excluded that reaction (1) in DMSO–AcOH takes several pathways, including that under the action of undissociated AcOH, which is responsible for the complicated nature of the concentration dependence of $k_{\mathrm{app}}$ (Fig. 2b).

According to [13], the dependence of the autoprotolysis constant $K_{\mathrm{ap}}$ on the composition of the DMSO–AcOH solvent is also complicated. The $K_{\mathrm{ap}}$ value decreases at low concentrations (up to 4.5 M) of each of the solvent components and reaches its maximum in the range 9–15 M AcOH. High $K_{\mathrm{ap}}$ values favor formation of species like $\mathrm{AcOH \cdot H^+}$ and $\mathrm{DMSO \cdot H^+}$ participating in solvoprotolytic dissociation [3] of porphyrin complexes [reaction (5)].

$$\mathrm{MP + 2H^+_{solv}} \xrightarrow{\mathrm{2X^-}} \mathrm{H_2P + MX_2}. \qquad (5)$$

It should be noted that the maximum on the concentration dependence of the dissociation rate constant of complex **IX** (Fig. 2) falls within the range of DMSO–AcOH compositions where $K_{\mathrm{ap}}$ is maximal [13]. Apparently, in this range of solvent compositions a near-optimal combination of the activity of attacking particles and the permittivity and ionizing power of the medium is reached. Variation of the DMSO–AcOH solvent properties produces the strongest effect with nonplanar complex **IX** and has almost no effect with compound (**VIII**).

Thus, in our opinion, one of the major reasons for the complication of the concentration dependence $k_{\mathrm{app}} = f(c_{\mathrm{AcOH}})$ for nonplanar compound **IX** is "admixing" acidoprotolytic dissociation under the action of undissociated AcOH. However, the acido-protolytic dissociation mechanism (4) cannot fully realize in the case of N-substituted MP. It is favored by the availability of the basic N-substituted atom to protonation, but conditions for further effective extra coordination of the anion on the metal atom and polarization of the particle are almost absent [11].

Thus, we showed that the disturbance of the planar structure of the ligands in Zn(II) porphyrin complexes has a negative effect both on the kinetic stability of the complexes in proton-containing media and on their resistance to thermooxidative degradation. Removal of the N-substituent from N-substituted porphyrins takes place not only in solution under action of organic bases, but also in the solid phase at elevated temperatures in the presence of air oxygen.

## EXPERIMENTAL

N-Substituted porphyrins and their zinc(II) complexes were prepared, purified, and identified according to the procedures [4, 14]. To remove traces of moisture and organic solvents, the samples were exposed to a vacuum at 80°C for 10 h before use. Pure grade solvents (DMSO and AcOH) were dried and additionally purified as recommended in [15].

Thermogravimatric studies were performed on an MOM-1000D derivatograph (Hungary). A crystalline sample of 40–50 mg was placed in a platinum crucible and heated in a static oxygen atmosphere at a rate of 5 $\deg \min^{-1}$ in the range of 15–1000°C. The sensitivity of the galvanometer for DTG was 1 mV and for DT, 250 mV, the sensitivity of the balances was 100 or 50 mg per 250 mm of the instrument scale. The error of measuring temperature was $\pm 0.5$°C, and the error of measuring sample weights was no less than $\pm 0.2$ mg.

Kinetic measurements in the course of dissociation reaction (1) in DMSO–AcOH or glacial AcOH were carried out on an SF-46 spectrophotometer by following the optical density at the experimental wavelength. The $\ln(c^0_{\mathrm{MP}}/c_{\mathrm{MP}}) = f(\tau)$ dependence for reaction (1) is rectilinear [Eq. (6)], which suggests that the reaction is first-order in metal complex. In Eq. (6), $k_{\mathrm{app}}$ is the apparent rate constant of reaction (1). The kinetic parameters ($E_a$ and $\Delta S^{\#}$) of reaction (1) were estimated using standard equations of formal kinetics.

$$-dc_{\mathrm{MP}}/d\tau = k_{\mathrm{app}}c_{\mathrm{MP}}. \quad (6)$$

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