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# Nucleophilicity of Heteroaromatic *N*-Oxides in Coordination with Zn(II) Tetraphenylporphyrinate and in the Substitution Reactions

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**Abstract**—Linear correlations have been revealed between thermodynamic and kinetic parameters of the nucleophilic substitution and coordination reactions of zinc(II) tetraphenylporphyrinate with heteroaromatic *N*-oxides in different solvents. Complex formation of zinc(II) tetraphenylporphyrinate with *n*-donor ligands in chloroform can serve as model system in spectroscopy studies of nucleophilicity and basicity of the compounds capable of the *n*,ν type complexes formation.

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This work extends the studies on correlation between the stability constants of zinc(II) tetraphenylporphyrinate complexes with various organic ligands and physicochemical parameters of the same ligands nucleophilic substitution reactions.

We have recently demonstrated [1, 2] that thermodynamic parameters of zinc(II) tetraphenylporphyrinate and zinc(II) protoporphyrinate dimethyl ester coordination with 3- and 4-substituted pyridines in chloroform linearly depend on the values of the bands shifts (Δλ) in electronic absorption spectra of these metal porphyrinates upon interaction with the pyridines as well as on p$K_a$ of the ligands in water, and on the Hammett constants σ of the substituents. The linear correlation between changes of enthalpy and entropy of the complexes formation confirms that the process is "isoequilibrium" or "isothermodynamic". Linear correlations have been found as well between thermodynamic and kinetic parameters of some nucleophilic substitution reactions of pyridines and complex formation reactions between zinc(II) tetraphenylporphyrinate and the pyridines.

Pyridines nucleophilicity is usually in line with reactivity of the corresponding pyridine *N*-oxides [3, 4]. In view of that, in this work we analyzed the kinetic and thermodynamic parameters of zinc(II) tetraphenylporphyrinate coordination with heteroaromatic pyridine-*N*-oxides (set **I**) and quinoline-*N*-oxides (set **II**) (Table 1). Taking into account the tabulated data, we will discuss some $S_N$ reactions of the above-listed ligands and their non-oxidized analogs (sets **III** and **IV**). Noteworthily, *N*-oxides of 2,6-dimethyl-4-nitropyridine (p$K_a$ –0.86 [5]), 2,6-dichloropyridine, and benzofuroxane (p$K_a$ of the latter pair were not found in the available literature; in the case of 2-chloropyridine-*N*-oxide, p$K_a$ was of –0.77 [6]) did not change the electron absorption spectrum of zinc(II) tetraphenylporphyrinate even when applied in the form of the saturated solutions in chloroform; that was evidently due to their extremely low nucleophilicity/basicity (see Scheme 1).

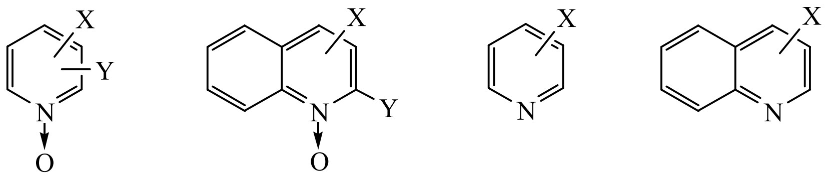
The measured stability constants *K* of zinc(II) tetraphenylporphyrinate complexes with heteroaromatic *N*-oxides in chloroform were, strictly speaking, the concentration ones. However, as the initial concentrations of the complex forming compounds were low ($2\times10^{-5}$ mol/L of zinc(II) tetraphenylporphyrinate and $10^{-4}$–$10^{-2}$ mol/L of the ligands) and the ionic forms were absent in the solution, the experimentally determined values should have been fairly close to the thermodynamic stability constants.

**Table 1.** Stability constants (*K*), thermodynamic parameters of the complex formation ($\Delta G^0$, $\Delta H^0$, $\Delta S^0$), shifts of I, II, and the Soret absorption bands ($\Delta\lambda$) upon the complex formation, σ and $\sigma_{PyO}$ constants of the substituents, and basicity ($pK_a$) of the ligands in water at 25°C; see complexes description in the text

| Ligand | $K_{298}$ | $pK_a$ (25°C) [7–9] | σ [12] | $\sigma_{PyO}$ [7] | Δλ Cope | $\Delta\lambda_{II}$ | $\Delta\lambda_I$ | $-\Delta H^0$, kJ/mol | $\Delta S^0$, J mol$^{-1}$ K$^{-1}$ | $\Delta G^0$, kJ/mol |
|---|---|---|---|---|---|---|---|---|---|---|
| **Ie** | 2470±63 | 2.05 | –0.268 | –0.603 | 10.2 | 14.5 | 17.0 | 13.94±0.26 | 19.0±0.8 | –19.35 |
| **Ib** | 1353±24 | 1.29 | –0.17 | –0.24 | 9.3 | 13.8 | 15.7 | 13.88±0.21 | 13.47±0.75 | –17.85 |
| **Ig** | 1272±24 | – | – | – | – | 13.8 | 15.4 | 13.66±0.03 | 13.23±0.1 | –17.70 |
| **Ia** | 816±35 | 0.79 | 0 | 0 | 8.8 | 13.3 | 15.0 | 13.43±0.39 | 10.6±0.6 | –16.60 |
| **Ii** | 609±14 | 0.36 | 0.227 | 0.206 | 8.4 | 12.6 | 13.8 | 13.81±0.37 | 7.1±0.6 | –15.88 |
| **Ih** | 134±2.5 | –1.7 | 0.778 | 1.19 | 5.3 | 10.0 | 12.0 | 13.74±0.15 | –5.71±0.4 | –12.13 |
| **It** | 1650±27 | 1.43 [10] | (–0.21) | (–0.40) | – | 14.1 | 16.3 | 13.90±0.31 | 15.16±0.8 | –18.35 |
| **Ir** | 1311±30 | 1.25 [10] | (–0.12) | (–0.26) | – | 13.6 | 15.8 | 13.83±0.25 | 13.23±0.7 | –17.77 |
| **Ip** | 1142±25 | 1.10 [10] | (–0.06) | (–0.16) | – | 13.4 | 15.6 | 13.81±0.22 | 12.47±0.4 | –17.44 |
| **Iv** | 1040±25 | 1.05 [10] | (–0.03) | (–0.11) | – | 13.0 | 15.2 | 13.77±0.44 | 11.7±0.8 | –17.20 |
| **Ic** | 1030±11 | 1.08 | –0.069 | –0.139 | 9.1 | 13.5 | 15.8 | 13.82±0.31 | 11.4±0.65 | –17.18 |
| **Ik** | 454±9 | – | 0.37 |  | 7.8 | 12.4 | 15.0 | 13.88±0.29 | 4.6±0.41 | –15.15 |
| **Iz** | 185±6 | –0.97 | 0.709[a] | 1.151[a] | 6.0 | 10.6 | 13.0 | 13.59±0.22 | –2.1±0.2 | –12.93 |
| **Iu** | 1495±29 | – | – | – | – | 14.1 | 16.1 | 13.83±0.28 | 14.22±0.9 | –18.10 |
| **Is** | 1215±25 | – | – | – | – | 13.6 | 15.7 | 13.69±0.16 | 13.40±0.7 | –17.59 |
| **Iq** | 1090±24 | – | – | – | – | 13.2 | 15.5 | 14.04±0.26 | 11.0±0.6 | –17.32 |
| **IIe** | 5522±136 | – | –0.268 | –0.603 | 10.4 | 14.7 | 17.4 | 13.90±0.29 | 25.3±1.2 | –21.34 |
| **IIb** | 3085±73 | 1.44 | –0.17 | –0.24 | 9.8 | 14.0 | 16.3 | 13.61±0.26 | 21.2±0.7 | –19.90 |
| **IIa** | 2326±72 | 0.86 | 0 | 0 | 9.2 | 13.3 | 15.7 | 13.81±0.34 | 18.1±0.95 | –19.20 |
| **IIj** | 2069±32 | 0.232 | – | – | – | 12.7 | 15.3 | 13.96±0.24 | 16.55±0.6 | –18.91 |
| **IIi** | 1600±31 | 0.47 | 0.227 | 0.206 | – | 11.8 | 14.6 | 13.74±0.11 | 15.00±0.7 | –18.27 |
| **IIh** | 267±9 | –1.39 | 0.778 | 1.19 | – | 9.3 | 12.1 | 13.50±0.24 | 1.41±0.46 | –13.86 |
| **Id** | 1237±32 | 1.02 | – | – | 9.0 | 13.3 | 15.9 | 11.91±0.03 | 19.2±0.45 | –17.63 |
| **Iy** | 189±5 | –0.967 | – | – | 5.8 | 10.4 | 12.9 | 11.85±0.29 | 5.40±0.4 | –12.87 |
| **IId** | 396±6 | – | - | – | – | 13.1 | 16.0 | 12.05±0.22 | 9.50 ±0.5 | –14.81 |
| **IIx** | 344±7 | – | – | – | – | 12.6 | 14.7 | 12.18±0.24 | 7.90±0.5 | –14.46 |
| **IIw** | 292±4 | – | – | – | – | 12.3 | 14.0 | 12.02±0.32 | 7.23±0.6 | –14.06 |
| **IIy** | 67.2±1.6 | – | – | – | – | 9.6 | 12.3 | 11.80±0.11 | –4.21±0.21 | –10.42 |
| **IIu** | 429±6 | – | – | – | – | 15.4 | 16.9 | 12.03±0.15 | 10.0±0.6 | –15.01 |
| **IIs** | 340±8 | – | – | – | – | 14.4 | 16.2 | 12.36±0.39 | 7.26±0.63 | –14.43 |
| **IIq** | 251±6 | – | – | – | – | 14.0 | 15.9 | 12.15±0.34 | 5.90±0.41 | –13.68 |
| **IIIa** | 3517±150 | 5.29 | 0 | – | 9.8 | 15.0 | 18.2 | 17.30±0.17 | 8.9±0.6 | –20.2 |
| **IVa** | 114±3 | 4.81 [11] | 0 | – | 8.5 | 14.7 | 16.3 | 14.58±0.14 | -9.81±0.6 | –11.73 |

[a] Σσ and $\Sigma\sigma_{PyO}$, respectively.

**Scheme 1.**



**Ia–Ie, Ig–Ii, Ik, Ip–Iw, Iy, Iz** **IIa, IIb, IId, IIe, IIh–IIj, IIq, IIs, IIu, IIw–IIy** **IIIa, IIIb, IIIf, IIIk–IIIo** **IVa**

Y = H, X = H (**a**), 4-Me (**b**), 3-Me (**c**), 2-Me (**d**), 4-MeO (**e**), 4-$NMe_2$ (**f**), 4-$N_3$ (**g**), 4-$NO_2$ (**h**), 4-Cl (**i**), 4-Br (**j**), 3-COOEt (**k**), 4-$CONHNH_2$ (**m**), 3-$CONH_2$ (**n**), 4-CN (**o**), 4-($C_6H_5CH$=CH) (**p**), 2-($C_6H_5CH$=CH) (**q**), 4-(4-$MeOC_6H_4CH$=CH) (**r**), 2-(4-$MeOC_6H_4CH$=CH) (**s**), 4-(4-$NMe_2C_6H_4CH$=CH) (**t**), 2-(4-$NMe_2C_6H_4CH$=CH) (**u**), 4-(4-$ClC_6H_5CH$=CH) (**v**); Y = 2-Me, X = 4-Cl (**w**), 4-Br (**x**), 4-$NO_2$ (**y**); Y = 3-Me, X = 4-$NO_2$ (**z**).

Similarly to the case of pyridines [1, 2], the steric factor being of minor significance, the logarithms of stability constant of zinc(II) tetraphenylporphyrinate complex with pyridine-*N*-oxides and quinoline *N*-oxides (**IIIa** > **IIa** > **Ia** > aniline > **IVa**) in chloroform were linearly correlated with p$K_a$ of the respective ligand in water, with the Hammett constant σ of the respective substituent, and with the bands shift (Δλ) of the electron absorption spectra (Table 1 and Fig. 1).

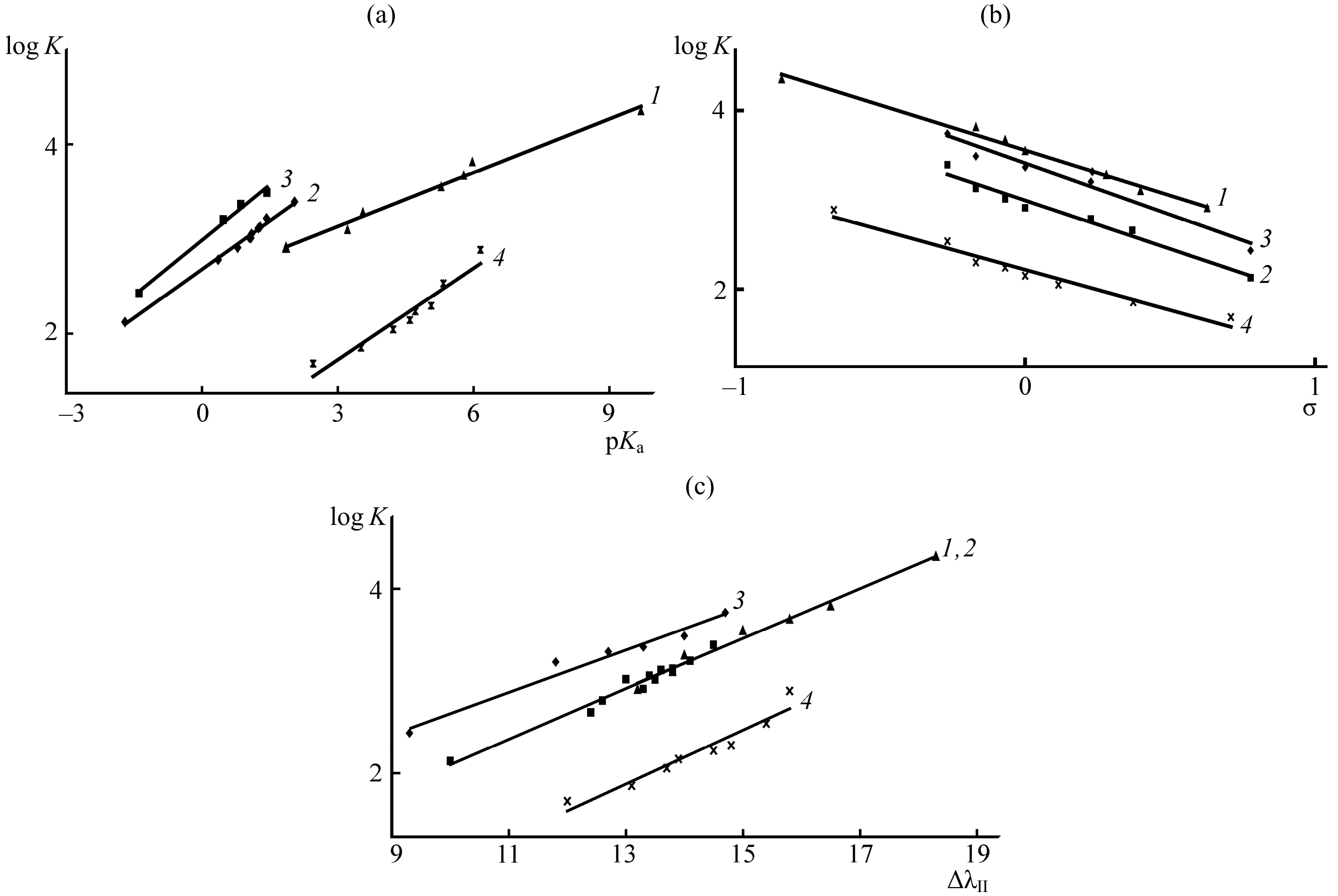


**Fig. 1.** Stability of the complexes of zinc(II) tetraphenylporphyrinate with 3- and 4-substituted pyridines [1] (*1,* triangles), pyridine-*N*-oxides (*2,* diamonds), quinoline-*N*-oxides (*3,* squares), and anilines [13, 14] (*4,* crosses) in chloroform at 298 K as functions of (a) p$K_a$ of the ligands in water, (b) the Hammett constant, and (c) absorption band II shift upon complexation.

The log $K$ – p$K_a$ and log $K$ – σ data were described with different linear equations within the sets of pyridines, pyridine-*N*-oxides, and quinoline-*N*-oxides (lines *1–3* in Figs. 1a and 1b). However, the log $K$ – Δλ dependences coincided in the cases of pyridines and pyridine-*N*-oxides (sets *1* and *2* in Fig. 1c); for example, in the case of band II, log $K = 0.272\Delta\lambda_{II} - 0.623$, $n = 18$, $r = 0.992$). In the cases of all the datasets, except for log $K$ – p$K_a$ data for pyridines, the lines slopes were close in the cases of ligands of different classes.

The higher activity in the nucleophilic substitution reactions (“supernucleophilicity”) of pyridine-*N*-oxides as compared to pyridines of close basicity is usually explained by better steric availability of the N→O group oxygen atom [3, 4] as compared to that of nitrogen atom in pyridines. However, the basicity of pyridines in water was much more sensitive ($\mathrm{p}K_a^{\mathrm{Py}} = -5.33\sigma + 5.23$) to the nature of heteroaromatic ring substituents than that of pyridine-*N*-oxides ($\mathrm{p}K_a^{\mathrm{PyO}} = -3.35\sigma + 0.93$); hence, the above-mentioned trend might be due to difference in hydration of the bases and their protonated forms [1]. Therefore, in order to correctly compare the complex formation ability of pyridines and the corresponding *N*-oxides, the zinc(II) tetraphenylporphyrinate complexes stability should have been measured in the same medium (chloroform was chosen in this work due to availability of experimental data). Unfortunately, the found p$K_a$ values of the studied compounds in chloroform were scarce; therefore, we used the available data on basicity in acetonitrile, another aprotic solvent. Analysis of the data in the log $K$ – p$K_a$(MeCN) coordinates revealed that [in contrast to the log $K$ – p$K_a$($H_2O$) plots] the pyridine complexes with zinc(II) tetraphenylporphyrinate were more stable than those of pyridine-*N*-oxides of the same basicity, the exceptions being only the ligands containing very strong electron-donating substituents (for instance, 4-dimethylaminopyridine, σ –0.84). To conclude, the term “supernucleophilicity” should not be used to discuss the complex formation of pyridine-*N*-oxides with zinc(II) tetraphenylporphyrinate. Moreover, the substituents in the aromatic rings being the same, the stability constants in the case of pyridine derivatives were always higher than those in the cases of pyridine-*N*-oxides.

The fitting lines *2–4* in Figs. 1a–1c were almost parallel. That fact could point at the similar mechanisms of coordination and protonation of heteroaromatic *N*-oxides and anilines, therefore, similarity in the mechanism of their nucleophilic substitution reactions $S_N$ could be assumed. At close basicity, the somewhat higher nucleophilicity of quinoline-*N*-oxides (log $K = 0.387\mathrm{p}K_a + 2.68$, $n = 4$, $r = 0.997$) as compared to that of pyridine-*N*-oxides (log $K = 0.339\mathrm{p}K_a + 2.68$, $n = 10$, $r = 0.991$) and of pyridines (log $K = 0.189\ \mathrm{p}K_a + 2.57$, $n = 7$, $r = 0.991$; in the case of quinoline, the data point was much lower than the fitting lines *1–3* in Fig. 1a) was seemingly due to special features of the above-mentioned heterocycles dynamic polarization upon interaction with acceptors of various Pearson hardness [15] in the protic and aprotic solvents ($H^+$ in water and zinc(II) tetraphenylporphyrinate in chloroform).

The slopes of the log $K$ – σ fitting lines (Fig. 1b) were not significantly different between the sets of pyridines (log $K = -1.01\sigma + 3.56$, $n = 7$, $r = 0.994$), pyridine-*N*-oxides (log $K = -1.09\sigma + 2.99$, $n = 7$, $r = 0.98$), quinoline-*N*-oxides (log $K = -1.15\sigma + 3.14$, $n = 6$, $r = 0.98$), and anilines (log $K = -0.85\sigma + 2.32$, $n = 14$, $r = 0.97$). As σ values depended exclusively on the nature of aromatic rings substituents, it was concluded that their coordination to zinc(II) tetraphenylporphyrinate in chloroform was not very sensitive to the (O,N) donor center type and to the aromatic system of the ligand.

Analysis of correlation of the complexes stability and their spectral properties (log $K$ – Δλ data, the both parameters were determined in chloroform medium) revealed that behavior of 3- and 4-substituted pyridines and pyridine-*N*-oxides could be fitted with the same equation (log $K = 0.272\Delta\lambda_{II} - 0.623$, $n = 19$, $r = 0.992$). Evidently, in the cases of those ligands, the steric effects on the complex formation and solvation in the low-polar solvent were similar, and the electronic spectra changes resulting from zinc(II) tetraphenylporphyrinate coordination were affected exclusively by the electron-donating properties of heteroatoms (oxygen or nitrogen) depending in turn on their polarizability and electronegativity as well as on the electronic effects of the substituents. In the case of quinolines and quinoline-*N*-oxides, the surrounding of nitrogen and oxygen atoms were much different, and the log $K$ – Δλ data were therefore fitted with other equations (Fig. 1c).

Conclusions on evaluation of the steric effects on the zinc(II) tetraphenylporphyrinate complex formation with heteroaromatic *N*-oxides were as follows. Contrary to the pyridines case [16], location of methyl substituent in pyridine-*N*-oxide slightly influenced the complexes stability constant (pyridine-*N*-oxide, $K$ = 816 L/mol; 2-methylpyridine-*N*-oxide, $K$ = 1237 L/mol; 4-methylpyridine-*N*-oxide, $K$ = 1353 L/mol, and 3-methylpyridine-*N*-oxide, $K$ = 1030 L/mol). Hence, the hyperconjugation effect of Me group in the positions 2 and 4 (in the case of 3-substituted ligand that effect was absent) affected the nucleophilicity of ligands more than its inductive and steric effects. Besides, in the cases of all the studied 2-, 3-, and 4-substituted pyridine-*N*-oxides (including styryl derivatives and 3-methyl-4-nitropyridine-*N*-oxide), the general equations ($\log K = 0.268\Delta\lambda_{II} - 0.556$, $n = 18$ $r = 0.99$ and $\log K = 0.358\mathrm{p}K_a + 2.66$, $n = 13$, $r = 0.994$) were held satisfactorily. Position of methyl group in the substituted quinoline-*N*-oxides affected more the studied coordination process. In particular, the complex stability constant was of $K$ = 2326 L/mol in the case of parent quinoline-*N*-oxide; that in the case of 4-methylquinoline-*N*-oxide ($K$ = 3085 L/mol) was higher and that in the case of 2-methylquinoline-*N*-oxide ($K$ = 396 L/mol) was much lower. Evidently, in the latter case, steric hindrance was extremely significant due to combined spatial influence of 2-Me and 8-H. Behavior of quinoline-*N*-oxides bearing 2-styryl substituents was somewhat special. Their coordination with zinc(II) tetraphenylporphyrinate was characterized by significantly lower stability constants, but it caused much stronger spectral changes (Δλ of chloroform solutions) than that of 2- and 4-styrylpyridine-*N*-oxides. Hence, on the contrary to the pyridine-*N*-oxides case (line *2* in Fig. 2), the data corresponding to quinoline-*N*-oxides was fitted by three different lines *1, 3*, and *4* (Fig. 2). That was probably due to special features of steric interaction of hydrogen atom, methyl and styryl groups in the position 2 of quinoline ring with the zinc(II) tetraphenylporphyrinate macrocycle in the course of the complex formation.

Probably, the measured stability constants of pyridine-*N*-oxides and quinoline-*N*-oxides complexes with zinc(II) tetraphenylporphyrinate corresponded to the *n*,ν type 1 : 1 molecular complexes with the dative O–Zn bond. In particular, the linear correlation between p$K_a$ in water and $\log K$ in chloroform (Table 1, Fig. 1a) along with the X-ray diffraction data for the isoquinoline-*N*-oxide complex with zinc(II) tetraphenylporphyrinate [9] confirmed that protonation and coordination of ligands **I** and **II** with metal porphyrinates proceeded via the same center, the N→O group oxygen atom.

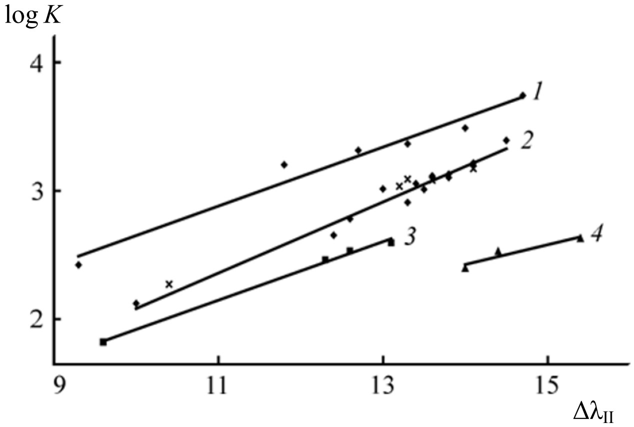


**Fig. 2.** Stability of the complexes of zinc(II) tetraphenylporphyrinate with 4-substituted quinoline-*N*-oxides (*1*), 2-, 3-, and 4-substituted pyridine-*N*-oxides (*2*), 4-substituted 2-methylquinoline-*N*-oxides (*3*), and 2-styryl-substituted quinoline-*N*-oxides (*4*) in chloroform at 298 K as function of the absorption band II shift upon complex formation. The symbols shape corresponds to that in Fig. 1.

Furthermore, we studied the structure of zinc(II) tetraphenylporphyrinate complex with 4-chloroquinoline-*N*-oxide by X-ray diffraction (Fig. 3). Data in Table 2 confirm that it was the axial 1 : 1 molecular complex.

The *dsp*$^2$ Zn atom was located in the porphyrin cycle plane the molecule of zinc(II) tetraphenylporphyrinate. In the course of 1 : 1 axial complex formation, the Zn hybridization was changed to *sp*$^3$*d*$^2$ [9]. The four hybrid orbitals were located in the porphyrin cycle plane, and the other two orbitals (the free and the ligand-binding) were normal to it.

In the complex of zinc(II) tetraphenylporphyrinate with 4-chloroquinoline-*N*-oxide, the coordination number of zinc equaled five, with tetragonal pyramid as coordination polyhedron (Fig. 3a). Zinc atom was off the base plane (determined by the porphyrin nitrogen atoms) by 0.28 Å and was located at 2.13 Å from oxygen atom. That was typical of such zinc coordination; for example, in the zinc(II) tetraphenylporphyrinate complex with 3-nitroaniline (Cambridge Structural Database reference code HAMLAI [17]) the off-plane distance was of 0.25 Å. The $L_2$ ligand (4-chloroquinoline-*N*-oxide) was disordered in such a way (Fig. 3b) that $L_2$ atoms of the both positions were located practically in the same plane (average deviation from the mean plane passing through all the non-hydrogen atoms of $L_2$ was of 0.03 Å, the largest deviation being of 0.12 Å). The angle between the planes of porphyrin and the ligands was of 26.58°.

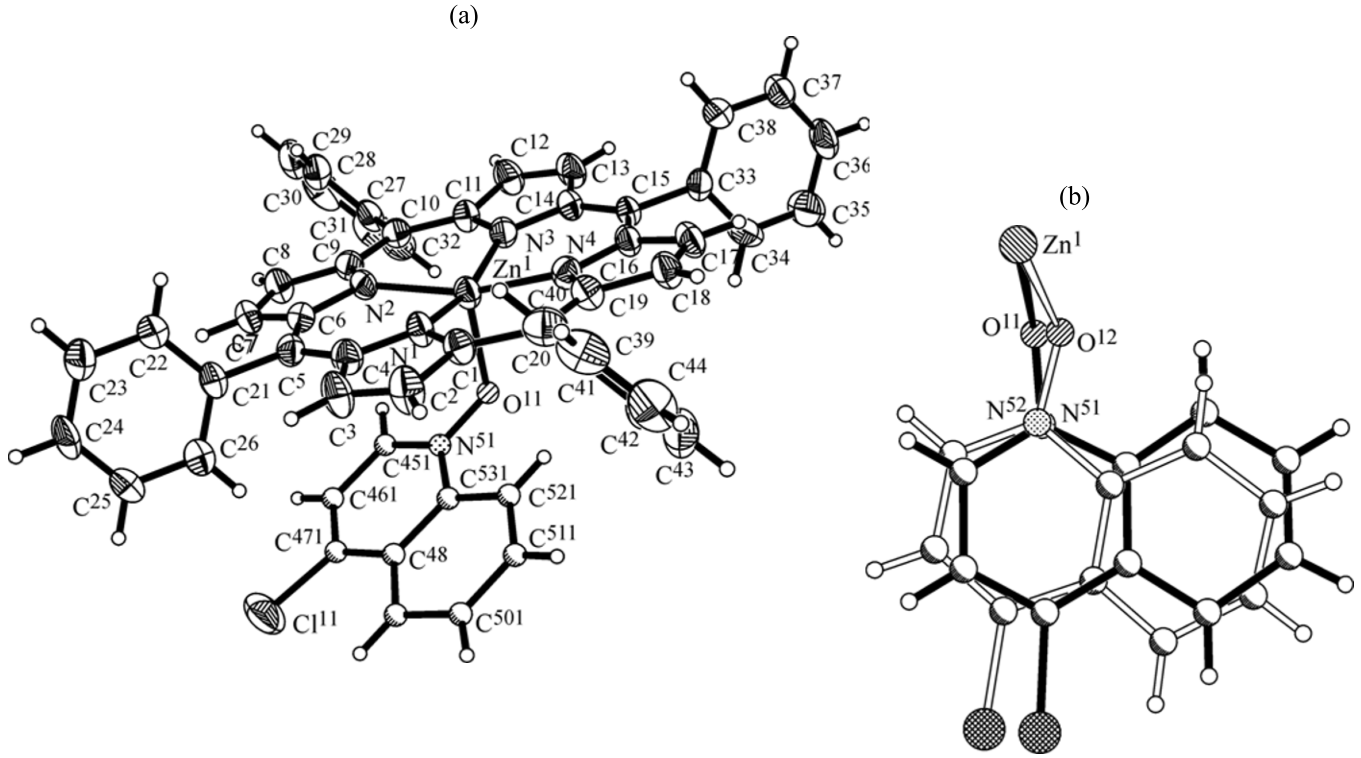


**Fig. 3.** (a) Structure of the 1 : 1 molecular complex of zinc(II) tetraphenylporphyrinate with 4-chloroquinoline-*N*-oxide **I** (one of the positions of disordered ligand $L_2$ is shown) and (b) scheme the disordering.

We failed to find any compounds containing the $L_2$ ligand in the Cambridge Structural Database [17] (version 5.32, August 2011). The geometry parameters were close to those of [Zn(2-methylquinoline-1-oxide)$_2$Cl$_2$]; in particular, the N→O bond length coincided with the data reported on the of *n*,ν type molecular complexes formed by heteroaromatic *N*-oxides [18].

Geometry of zinc(II) tetraphenylporphyrinate complex with 4-chloroquinoline-*N*-oxide most likely corresponded to the $sp^3$ hybridization state of oxygen because the angle between the plane of heterocycle and the plane of the NOZn fragment ruled out the conjugation of oxygen atom with heterocyclic ring as well as with the metal ion.

Using the above-derived linear equations of log $K = f(\sigma^{\mathrm{PyO}})$, we calculated the σ constants of styryl substituents (Table 1, in parentheses). From the result it followed that upon coordination of zinc(II) tetraphenylporphyrinate with the **Ip, Ir, It,** and **Iv** ligands, the electronic effects of $NMe_2$ and OMe groups in *p*-position of benzene rings were weakened by the –CH=CHPh conjugated system. Hence, the $\sigma_p$ values of *p*-$Me_2NC_6H_4CH{=}CH$ and *p*-$MeOC_6H_4CH{=}CH$ were of –0.21 and –0.12, respectively. The chlorine atom of the styryl fragment (evidently being weaker electron acceptor than the N→O group and being conjugated with the latter) became the electron-donating group as well, due to its +*M*-effect ($\sigma_{\mathrm{PyO}}$ –0.11). However, its effect was weaker than that of unsubstituted styryl group ($\sigma_{\mathrm{PyO}}$ –0.16).

As the structure of zinc(II) tetraphenylporphyrinate complexes with heteroaromatic *N*-oxides was similar to that of the $S_N$ reactions transition states [5] (the *N*-oxides acting as nucleophile), we evaluated the correlation between the parameters characterizing those processes. Examples of linear correlations between rate constants of five nucleophilic substitution reactions log *k* in acetonitrile and dichloromethane with log *K* and Δλ of the corresponding zinc(II) tetraphenyl-porphyrinate complexes with 3- and 4-substituted pyridine-*N*-oxides are collected in Table 3.

Hence, the rate constant of nucleophilic substitution reactions in different organic solvents could be calculated from the *K* and Δλ values using the nucleophilicity/basicity scale offered in [16]; reverse calculation was possible as well. Importantly, similar trends were revealed in the cases of 2-, 3-, and 4-methylpyridine-*N*-oxides coordination with zinc(II) tetraphenylporphyrinate as well as in the cases of their $S_N$ reactions [24]. Therefore, we concluded that the steric effects of methyl group were insignificant. However, that was not the case of styryl derivatives [23]. Stability of zinc(II) tetraphenylporphyrinate complexes with compounds **It** and **Iu** was almost equal, but the corresponding equilibrium constants of acyl group transfer [Table 3, reaction (5)] differed by almost an order of magnitude. Evidently, that was due to more strict steric demands for formation of pentacoordinated $S_N$ reactions transition state than those in the case of 1 : 1 *n*,ν complex with planar molecule of metal porphyrin.

It was natural to expect the linear correlation between thermodynamic parameters of the studied nucleophilic reactions and complex formation. We calculated thermodynamic parameters of their formation from the measured values of stability constants of zinc(II) tetraphenylporphyrinate complexes with heteroaromatic *N*-oxides at different temperatures (273–313 K) (Table 1).

$\Delta H^0$ values in all the cases were negative. In the cases of 3- and 4-substituted pyridine-*N*-oxides, 2-styryl substituted pyridine-*N*-oxides, and 4-substituted quinoline-*N*-oxides, the values were close (–13.50 to –14.04 kJ/mol, $\Delta H^0_{\text{average}}$ –13.78±0.15 kJ/mol, $n$ = 22, series A). In the cases of *N*-oxides of 2-methylpyridine, 2-methylquinoline, and 2-styrylquinoline, $\Delta H^0$ values were close as well, however, the average value was different (–11.80 to –12.36 kJ/mol, $\Delta H^0_{\text{average}}$ = –12.04±0.18 kJ/mol, $n$ = 9, series B). Hence, within the both series of heteroaromatic *N*-oxides (similarly to 3- and 4-substituted anilines with $\Delta H^0_{\text{average}}$ of –14.6±0.14 kJ/mol [1]) the coordination with zinc(II) tetraphenylporphyrinate was isoenthalpic. Noteworthily, in the case of pyridines, $\Delta H^0$ values were variable and linear with the ligand basicity [1].

$\Delta S^0$ as well as $\Delta G^0$ values of formation of zinc(II) tetraphenylporphyrinate complexes with *N*-oxides of 3- and 4-substituted pyridines ($\Delta S^0 = 6.67\text{p}K_a + 4.96$, $n$ = 11, $r$ = 0.998) and quinolines ($\Delta S^0 = 7.12\text{p}K_a + 11.47$, $n$ = 4, $r$ = 0.999) in chloroform (Fig. 4) were proportional to the ligands basicity and Hammett constants σ. Thus, despite enthalpy control of coordination process ($\Delta S^0$ gave the major contribution to $\Delta G^0$), the selectivity of complexes formation (dependence of *K* value on the *N*-oxides structure similarly to the case of anilines [13]) was determined by the entropy effects. In the case of zinc(II) tetraphenylporphyrinate coordination with pyridines [1, 2], $\Delta S^0$ was linear with the ligand basicity (and with $\Delta H^0$) as well, but the values were more variable (–27 to +54 J mol$^{-1}$ K$^{-1}$).

**Table 2.** Selected geometry parameters of complex **I** (bond lengths, Å and bond angles, deg)[a]

| Bond | *d*, Å | *n* = 1 | *n* = 2 |
|---|---|---|---|
| Zn$^1$–N$^3$ | 2.049(4) | | |
| Zn$^1$–N$^4$ | 2.057(4) | | |
| Zn$^1$–N$^1$ | 2.066(3) | | |
| Zn$^1$–N$^2$ | 2.075(4) | | |
| Zn$^1$–O$^{1n}$ | | 2.126(11) | 2.130(7) |
| O$^1$–N$^{5n}$ | | 1.332(9) | 1.356(10) |
| Cl$^{1n}$–C$^{47n}$ | | 1.737(8) | 1.741(10) |
| N$^{5n}$–C$^{45n}$ | | 1.336(10) | 1.324(11) |
| N$^{5n}$–C$^{53n}$ | | 1.381(10) | 1.400(11) |
| C$^{45n}$–C$^{46n}$ | | 1.412(11) | 1.419(14) |
| C$^{46n}$–C$^{47n}$ | | 1.352(13) | 1.355(15) |
| C$^{47n}$–C$^{48n}$ | | 1.407(13) | 1.388(16) |
| C$^{48n}$–C$^{49n}$ | | 1.373(11) | 1.363(15) |
| C$^{48n}$–C$^{53n}$ | | 1.418(11) | 1.419(14) |
| C$^{49n}$–C$^{50n}$ | | 1.456(13) | 1.483(17) |
| C$^{50n}$–C$^{51n}$ | | 1.397(13) | 1.371(17) |
| C$^{51n}$–C$^{52n}$ | | 1.384(10) | 1.401(14) |
| C$^{52n}$–C$^{53n}$ | | 1.385(12) | 1.383(14) |

[a] Bond angles, ω: O$^{12}$Zn$^1$O$^{11}$ 10.2(4), $n$ = 1; N$^{5n}$O$^{1n}$Zn$^1$ 113.5(11), $n$ = 1; 116.7(11), $n$ = 2.

The $\Delta S^0$ decrease with the decreasing of electron-donating ability of the heteroaromatic *N*-oxide ligands (similarly to the case of primary anilines [14]) could be at least partially due to the gradual increase of *p*-character of the lone-electron pair of nitrogen atom with shifting the electron density towards benzene ring (and, therefore, the change of $sp^3$ hybridization into $sp^2$ one).

As expected, the stability constants of zinc(II) tetraphenylporphyrinate complexes increased with decreasing temperature. The plots of $\Delta G$ as function of *T* (Fig. 5) revealed that at approximately 40 K the complexes stability should have become independent

**Table 3.** Nucleophilic substitution reactions with lg$k$ values linearly ($r$ = 0.97–0.999) correlated with lg$K$ and $\Delta\lambda$ of complex formation; see detailed description in the text

| Reaction no. | Reaction | Conditions |
|---|---|---|
| 1 | $R^1C_5H_4N{\rightarrow}O + R^2X \rightarrow R^1C_5H_4NOR^2X$<br>$R^1$ = H, 4-Me, 4-MeO; $R^2$ = Me, Et, $PhCH_2$; X = I, Br | Acetonitrile,<br>25°C [19] |
| 2 | $R^1C_5H_4N{\rightarrow}O + R^2X \rightarrow R^1C_5H_4NOR^2X$<br>$R^1$ = H, 4-Cl, 4-Me, 4-MeO; $R^2$ = Me, Et, *i*-Pr; X = I, Br | Acetonitrile,<br>25°C [20] |
| 3 | $R^1C_5H_4N{-}OAc + R^2C_5H_4N{\rightarrow}O \rightarrow R^1C_5H_4N{\rightarrow}O + R^2C_5H_4N{-}OAc$<br>$R^1$, $R^2$ = H, 4-Cl, 4-Me, 4-MeO | Acetonitrile,<br>дихлорметан,<br>25°C [21, 22] |
| 4 | $Me_2NCO(R^1C_5H_4N{\rightarrow}O)^+BPh_4^- + R^2C_5H_4N{\rightarrow}O \rightleftarrows Me_2NCO(R^2C_5H_4N{\rightarrow}O)^+BPh_4^- + R^1C_5H_4N{\rightarrow}O$<br>$R^1$, $R^2$ = H, 4-Me, 4-MeO, 3-Me, 4-$NC_4H_8O$, 4-(4-$Me_2NC_6H_4CH{=}CH$) | Acetonitrile,<br>25°C [10] |
| 5 | $AcCl + RC_5H_4N{\rightarrow}O \rightleftarrows RC_5H_4N^+{-}OAc + Cl^-$<br>$BzCl + RC_5H_4N{\rightarrow}O \rightleftarrows RC_5H_4N^+OBz + Cl^-$<br>R = H, 4-Cl, 4-Me, 4-MeO, 4-(4-$NMe_2C_6H_4CH{=}CH$), 4-$Me_2N$,<br>2-(4-$Me_2NC_6H_4CH{=}CH$), 4-$C_6H_4CH{=}CH$), 2-Me, 4-$NC_4H_8O$ | Acetonitrile,<br>Dichloromethane,<br>15–35°C<br>[23–25] |

of the ligand structure ($\Delta G$ being of –13.78 and –12.04 kJ/mol in the cases of ligands series A and B, respectively), provided that the trends revealed in the case of solutions were still operative. Similar conclusions followed from the analysis of corresponding data in the cases of aniline [14] and pyridine [1] ligands; in the latter case the critical temperature was of at 196 K.

The slopes of $\Delta G$ plots as function of $T$ with various Hammett constants suggested that at certain $\Sigma\sigma$ value ($\Sigma\sigma$ of 0.7–0.8 in the case of series A) $\Delta G$ of the process should be temperature-independent; indeed, that was observed in the case of 4-nitroquinoline-*N*-oxide ($\sigma$ = 0.778) (Fig. 5).

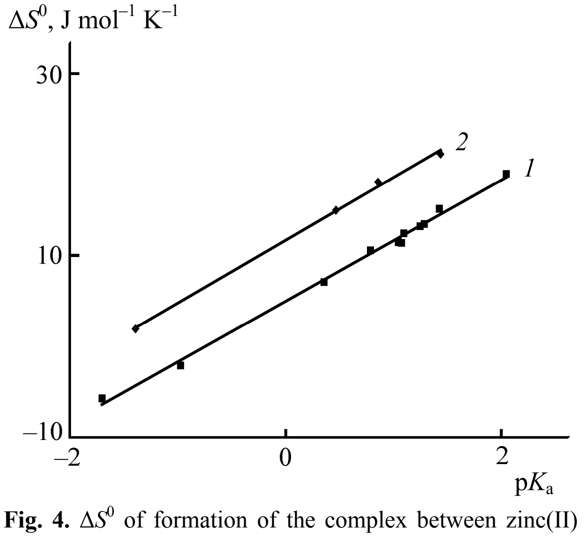


**Fig. 4.** $\Delta S^0$ of formation of the complex between zinc(II) tetraphenylporphyrinate and 3- or 4-substituted pyridine-*N*-oxides (*1*) and quinoline-*N*-oxides (*2*) in chloroform as function of p$K_a$ of the ligands in water at 25°C.

According to the X-ray diffraction data collected on crystals [26], zinc(II) tetraphenylporphyrinate complexes with heteroaromatic *N*-oxides and anilines were of molecular 1 : 1 *n*,ν-type with the angle between metal porphyrin plane and the ligand aromatic ring of 24°–34°. In the similar complexes, pyridines were oriented almost perpendicularly (with the angle of 80°–89°) to the porphyrin plane. Seemingly, those structural differences caused the different in thermodynamics and kinetics of pyridines coordination to zinc(II) tetraphenylporphyrinate as compared with that of anilines and heteroaromatic *N*-oxides.

To conclude, heteroaromatic *N*-oxides behavior in the $S_N$ reactions as well as in the coordination processes (in particular, the linear correlations between log $K$, log $k$, p$K_a$, and $\sigma$ constants) was quite similar to that of the non-oxidized analogs. However, thermodynamics of Zn(II) tetraphenylporphyrinate complexes formation revealed some differences between the ligands. In the cases of pyridines, the process was isoequilibrium, whereas in the cases of pyridine-*N*-oxides and quinoline-*N*-oxides it was isoenthalpic (similarly to the cases of anilines). The latter group of ligands could be divided into two series according to the $\Delta H$ values. Series A included 3-and 4-substituted ligands and pyridine-*N*-oxides containing 2-styryl substituents. Series B consisted of 2-methyl-substituted ligands and quinoline-*N*-oxides containing 2-styryl substituents.

The special features of the second series was seemingly due to different steric hindrances in the cases of 2-styrylpyridine *N*-oxides (planar molecules) and 2-methyl derivatives (with $sp^3$ carbon atom) and 2-styrylquinoline-*N*-oxides (with 8-H and 2-styryl substituents preventing the location of two $sp^2$ oxygen orbitals in the heterocycle plane).

When planning the research, we expected that analysis of thermodynamic parameters of nucleophilic substitution reactions of heteroaromatic *N*-oxides would explain the difference in thermodynamic behavior of pyridine-*N*-oxide and heteroaromatic *N*-oxides. However, the scarce data on pyridine-*N*-oxides [20–25] (for quinoline-*N*-oxides, no data was found) revealed that in all the cases the linear correlations between $\Delta H^\#$ and $\Delta S^\#$ or between $\Delta G^\#$ and $\Delta S^\#$ were fulfilled, meaning that the reactions were isokinetic.

We expect that the evaluation of limits of analogies between complex formation and chemical reactions of the same organic compounds will clarify the underlying mechanisms.

## EXPERIMENTAL

Pyridine-*N*-oxides and quinoline *N*-oxides [9, 27, 28] and styryl derivatives [29–31] were prepared as described in the above-cited works, the products physical constants agreed with the reference data.

Electron absorption spectra were recorded SF 2000–02 spectrophotometer. Stability constants of zinc(II) tetraphenylporphyrinate complexes with pyridine-*N*-oxides in chloroform (previously estimated from KFK-3 photocolorimeter data [32]) were evaluated with higher accuracy and processed according to [1]. Thermodynamic constants of complex formation were determined graphically using the equation below (as the first approximation, in the narrow temperature range of 273–313 K the $\Delta H$ and $\Delta S$ values were considered constant [33]).

$$\ln K_\mathrm{T} = -\Delta H^0_{298}/RT + \Delta S^0_{298}/R.$$

**Synthesis of [$ZnL_1L_2$], $L_1$: 5,10,15,20-tetraphenylporphyrin, $L_2$: 4-chloroquinoline-*N*-oxide (I).** Acetone solutions of zinc(II) tetraphenylporphyrinate ($5\times10^{-5}$ mol/L) and 4-chloroquinoline-*N*-oxide ($5.5\times10^{-5}$ mol/L), saturated at boiling point, were mixed, and the formed precipitate was centrifuged off, washed with acetone (3×2 mL), and dried in air.

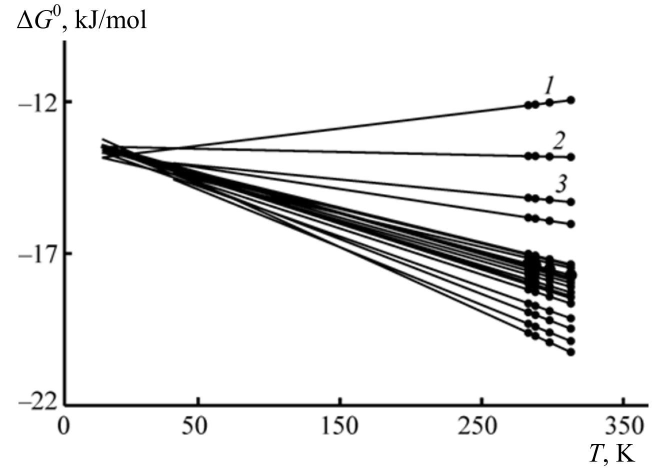


**Fig. 5.** $\Delta G$ of formation of the complex between zinc(II) tetraphenylporphyrinate and pyridine-*N*-oxides or quinoline-*N*-oxides in chloroform as function of temperature. (*1*) 4-NPyO, (*2*) 4-NQO, and (*3*) 3-COOEtPyO.

X-ray diffraction data on compound **I** ($C_{53}H_{34}ClN_5OZn$, $M$ = 857.67) was collected with Bruker APEX2 diffractometer [34] (Mo-Kα radiation, graphite monochromator, φΦ and ω scanning, room temperature). Red crystal of 0.15×0.09×0.04 mm. Triclinic, P-1 space group, $a$ = 10.3815(10) Å, $b$ = 13.0004(12) Å, $c$ = 15.8764(15) Å, $\alpha$ = 104.196(2)°, $\beta$ = 95.096(2)°, $\gamma$ = 101.090(2)°, $Z$ = 2, $V$ = 2017.6(3) Å$^3$, $d_\mathrm{calc}$ = 1.412 g/cm$^3$, $\mu$ = 0.724 mm$^{-1}$, $F$(000) = 884, $2\theta_\mathrm{max}$ = 50°, $-12 \le h \le 12$, $-15 \le k \le 15$, $-18 \le l \le 18$; 16756 reflections were collected in total, 7111 of them being independent ($R_\mathrm{int}$ = 0.0768), 3822 independent reflections with $I > 2\sigma(I)$ were registered. Absorption was accounted for semiempirically according to the equivalents (SADABS software [35]).

The structure was solved by combination of direct method and the differential Fourier syntheses (all calculations were carried out in SHELXS-97 and SHELXL-97 programs [36]). The $L_2$ ligand was disordered between two positions in the 3 : 2 ratio. The population value was refined in the course of isotropic refining of structure with fixed thermal parameters of $L_2$ atoms and was left constant in further refinement. Hydrogen atoms of ligands were located from geometry considerations. The structure was refined by means of full-matrix mean squares method ($F^2$) in the anisotropic-isotropic (O, N, and C atoms of the disordered $L_2$ ligand) approximation accounting for hydrogen atom in *rider* model with thermal parameters

20% higher than the equivalent thermal parameters of the adjacent carbon atoms. In the course of refinement, the SAME card of SHELXL-97 program was used for the ligand $L_2$. Refining results (548 parameters, 43 limitations on the bond lengths) were as follows: $R_1 = 0.0566$, $wR_2 = 0.1071$ over the reflections with $I > 2\sigma(I)$; $R_1 = 0.1296$, $wR_2 = 0.1351$ over all reflections, $GOF = 0.957$, maximum and minimum peaks in the zero Fourier synthesis 0.404 and –0.410 $e$/Å$^3$. Structure data were deposited in a Cambridge banc of structure data, CCDC 846681.

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