ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 4, pp. 738–743. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © S.V. Zaitseva, S.A. Zdanovich, O.I. Koifman, 2013, published in Zhurnal Obshchei Khimii, 2013, Vol. 83, No. 4, pp. 656–661.

Intermolecular Interactions of (5,15-Diphenyl-3,7,13,17-tetramethyl-2,8,12,18-tetrabutylporphyrinato)manganese Acetate with Small Organic Molecules

S. V. Zaitseva[a], S. A. Zdanovich[a], and O. I. Koifman[a,b]

[a] *Krestov Institute of Solution Chemistry, Russian Academy of Sciences, ul. Akademicheskaya 1, Ivanovo, 153045 Russia*
e-mail: svz@isc-ras.ru

[b] *Ivanovo State Chemical Technological University, Ivanovo, Russia*

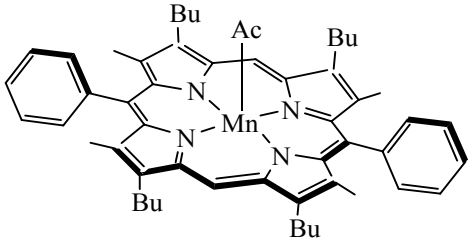
Received March 23, 2012

Abstract—The coordination properties of (5,15-diphenyl-3,7,13,17-tetramethyl-2,8,12,18-tetrabutylporphyrinato)-manganese(III) acetate toward small organic molecules in an inert solvent medium were studied. The values of the equilibrium constants of the process and the composition of the molecular complex were determined. The influence of the electronic and conformational factors of macrocycle on the value of the equilibrium constant was found. The geometry of isolated molecules of manganese porphyrinate and its molecular complexes was optimized by the quantum-chemical PM3 method. The structure of the reaction products favorable by the energy was theoretically found. A good agreement between the calculated and experimental data was obtained.

DOI: 10.1134/S1070363213040221

Currently one of the most important problems in modern chemistry is the study of the effects of the molecular recognition and the formation of the complex spatial self-organized structures with the desired properties. From this point of view the metal porphyrinates can be successfully used to create high-performance receptors, molecular switches, catalytic materials for industrial processes [1–3]. However, a search is actual for systems and the environment in which these macrocyclic compounds can exhibit the highest activity. Systematic studies on the synthesis and coordination chemistry of the metal porphyrinates promise to find the solution of this problem by modifying the structure and obtaining new compounds of this group. Therefore, within the study of the coordination properties of the highly charged metal cations, the intermolecular interaction of manganese(III) porphyrinate (Ac)MnP with organic bases L [1-methylimidazole (1-MeIm), imidazole (Im), 2-methylimidazole (2-MeIm), pyridine (Py), 4,4'-bipyridyl (BiPy), dimethylformamide (DMF)] in benzene at 298 K was examined.

The intermolecular interaction of manganese porphyrinate with the organic bases L was studied by the spectrophotometry [4, 5] and computer simulation [6–8]. The analysis of the quantum chemical calculations showed that the isolated molecule of manganese porphyrinate of a C_{4v} symmetry is sterically strained and predominantly has a saddle-shaped type of strain. The metal atom is significantly out of the N^4 plane. The average value of the deviation of the scaffold atoms of macrocycle from its *xy* average planealong a *z* axis is 0.63 Å.



The formation of the Mn–L bond is accompanied by a change in the steric strain of the macrocycle (Table 1, Fig. 1). The strain type and symmetry are retained. The existence of a molecular complex of (Ac)Mn(L)P type, where the base is coordinated by the acetate ion (Fig. 2), is favorable by energy. In the case of imidazole manganese porphyrinate one or two molecules can coordinate. Thus, there form 1:1 or 1:2 complexes.

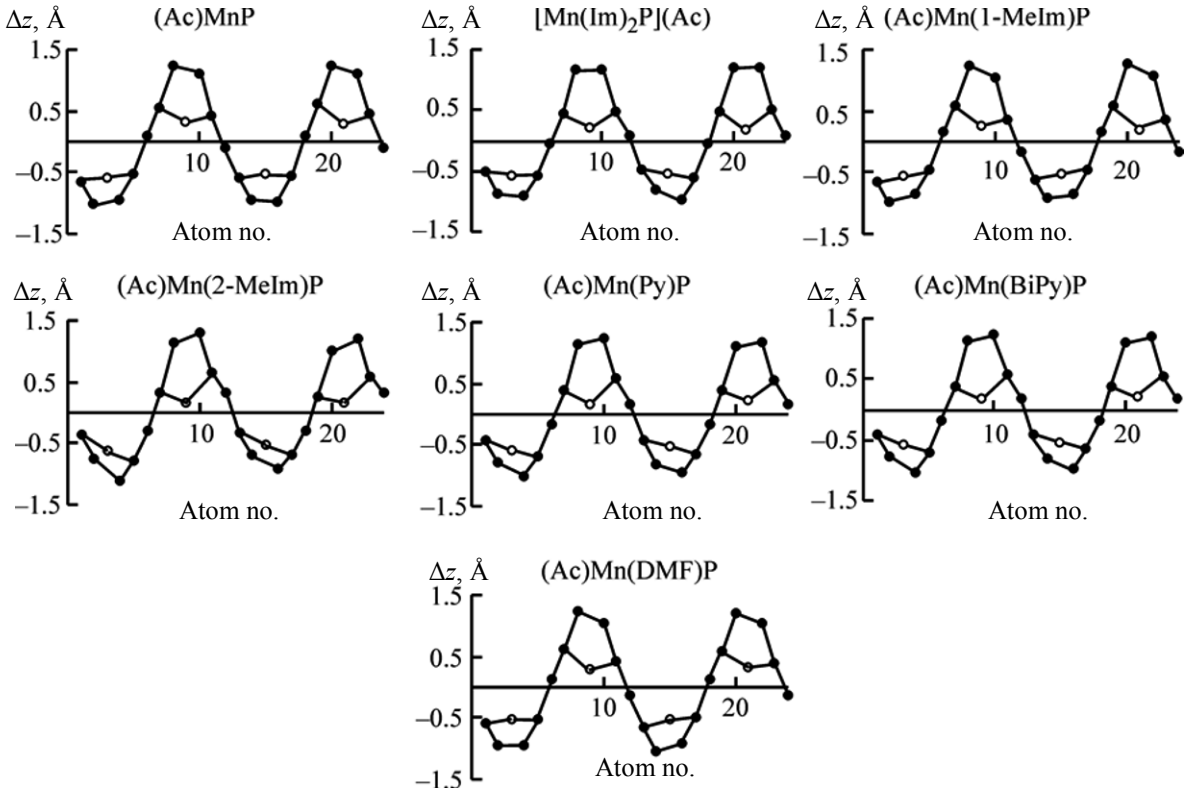


Fig. 1. Deviation of the skeletal atoms of the porphyrin macrocycle along a *z* axis from its average plane for (5,15-diphenyl-3,7,13,17-tetramethyl-2,8,12,18-tetrabutylporphyrinato)manganese(III) acetate and its molecular complexes according to the quantum-chemical calculation by the PM3 method. (Open circles) the nitrogen atoms, (dark circles) the carbon atoms.

The average value of the deviation of the skeletal atoms from the mean plane of the molecule for the molecular complexes changes by 0.02–0.03 Å. The deviation of the metal cation from the N^4 (Mn–Ct) plane increases.

The Mn–L bond is stronger as the basicity of the small organic molecule increases (Table 1). As the basicity parameter of the ligand L we take the pK_a values [9] and the estimated value of the protonation

Table 1. Some geometric and energy characteristics of (Ac)MnP and its molecular complexes

Complex	$-E_b$, kcal mol^{-1}	Bond length, Å						
		Mn–N_1 Mn–N_3	Mn–N_2 Mn–N_4	N_1–N_3 N_2–N_4	l_{Mn-L}	Mn–Ct	Mn–Ac	P[a]
(Ac)MnP		1.822 1.884	1.992 1.914	3.278 3.907		0.865	1.944	10.80
[MnP(Im)$_2$P](Ac)	92.15 65.87	1.874 1.935	1.966 1.962	3.344 3.915	1.925 1.991	0.932	–	10.73
(Ac)Mn(1-MeIm)P	77.89	1.850 1.922	1.988 1.941	3.344 3.923	1.919	0.895	2.127	10.75
(Ac)Mn(2-MeIm)P	80.08	1.918 1.858	2.012 1.925	3.326 3.925	1.909	0.913	2.146	10.65
(Ac)Mn(BiPy)P	71.04	1.918 1.858	2.010 1.941	3.323 3.940	1.921	0.946	2.145	10.74
(Ac)Mn(Py)P	67.97	1.916 1.860	2.010 1.940	3.233 3.940	1.927	0.952	2.144	10.72
(Ac)Mn(DMF)P	9.95	1.870 1.831	1.880 1.993	3.192 3.882	2.366	0.964	1.913	10.70

[a] The perimeter of the coordination plane N^4.

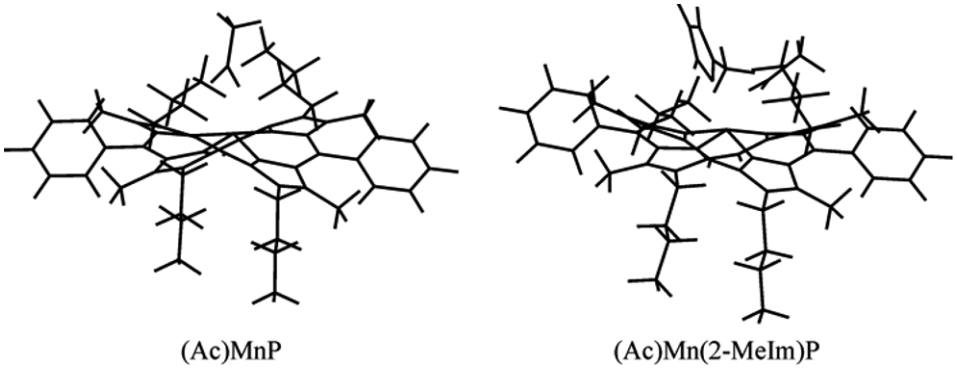


Fig. 2. The structure of isolated molecule of (Ac)MnP and its molecular complex with 2-methylimidazole calculated by the quantum-chemical method PM3.

energy E_{prot} characterizing the proton affinity of the base (Table 1) [10].

The spectrophotometric study of the coordination of *meso*-diphenyloctaalkyl-substituted manganese porphyrinate with the *N*-bases showed that in the complex formation the spectral changes are accom-panied with the retention of the isobestic points (Fig. 3). The titration curve is represented by a smoothly upward (on increasing wavelength) and smoothly downward (on lowering wavelength) line. However, the absorption spectra of the metal porphyrinates containing one or two additional ligands are very similar. In many cases there is no visible shift of an isosbestic point.

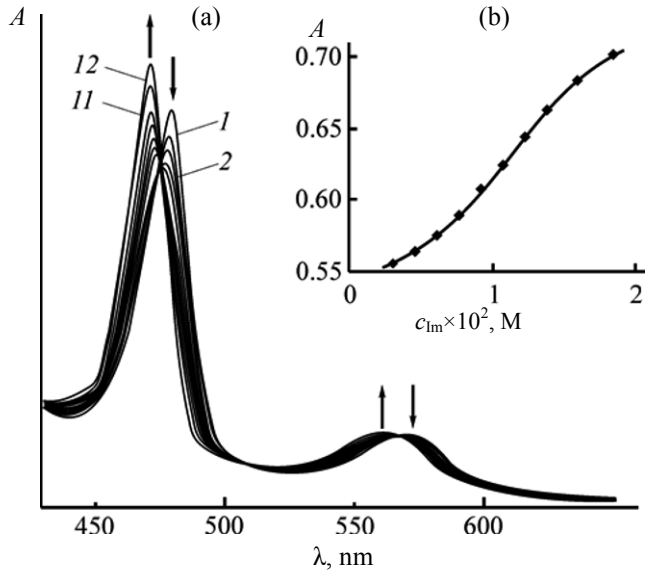


Fig. 3. Changing EAS of (Ac)MnP in the reaction with imidazole: (*1*) (Ac)MnP [$c_{(Ac)MnP}$ 3.87×10^{-6} M]; (*2–11*) (Ac)MnP with the intermediate concentrations of imidazole (c_{Im} 3.08×10^{-3}–1.85×10^{-2} M); (*12*) (Ac)MnP with an imidazole excess (c_{Im} 2.46×10^{-2} M) in (a) benzene and (b) the corresponding titration curve, λ 470 nm.

Therefore, the limiting logarithmic method was used for accurate determination of the composition of the molecular complex [4].

A number of ligands attached was determined by the slope of the linear $\log c_L$ dependence of log $[(A_{mix} - A_0)/(A_\infty - A_{mix})]$ (Fig. 4). The reaction products are (Ac)Mn(L)P. The exception is the complex with imidazole, where the addition of two molecules of the base and displacement of the acetate ion into the outer coordination sphere is observed. The composition of this complex is 1:2. The coordination of the base with the manganese porphyrinate is confirmed by the change in the ^{1}H NMR spectrum. The ^{1}H NMR spectra of a number of the high-spin manganese(III) porphyryinates are characterized by a significant broadening and large shifts of the signals, especially for *meso*- and pyrrole protons, compared with the spectra of the diamagnetic complexes [11–13]. In this case, the signal of the *meso*-H atom appears at 39 ppm. The formation of the mixed-ligand complex leads to a significant downfield shift of the signal of *meso*-protons to 45–51 ppm (Fig. 5). Such shift of a signal can be associated with an increase in the deviation of the metal atom from the N^4 plane due to the coordination of additional ligands from the acetate ion side. The interpretation of the other signals of the ^{1}H NMR spectrum is difficult, because the low symmetry of the ligands affects the resolution of the spectra.

The regularities of basicity change in small molecules in inert organic solvents are known to be retained in the gas phase [10]. Therefore, the study of the reaction requires using the calculated values of E_{prot} for the bases. It was found that the donor-acceptor properties of 2-MeIm and BiPy vary in passing from aqueous to an organic medium (Table 1). Analysis of

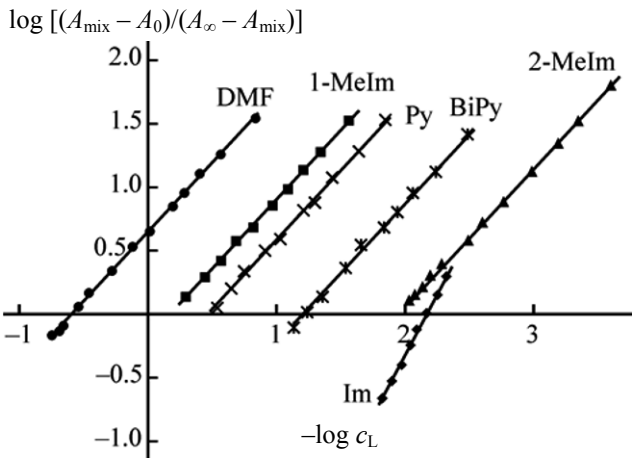


Fig. 4. The dependence of log $[(A_{mix} - A_0)/(A_\infty - A_{mix})]$ on log c_L for the reaction of (Ac)MnP with organic bases. (A_0, A_{mix}, A_∞) optical densities of the solutions at the working wavelength for the metal porphyrinate, equilibrium mixture, and the molecular complex.

the data in Table 2 indicates the linear dependence between the stability of the molecular complexes and values of pK_a and E_{prot} with the correlation equations log K_s = –0.052E_{prot} – 7.415 (r 0.99) and log K_s = 0.251pK_a – 0.145 (r 0.90), respectively (Fig. 6).

A good agreement between the values of K_s, the binding energy of the manganese atom with the nitrogen atom of the base (E_b), and the Mn–L bond length ($l_{Mn–L}$) (Fig. 7, Tables 1, 2). The variations occur in the same direction and are described by the correlation equations: log K_s = 0.019$e^{-0.056E_b}$ (r 0.99) and log K_s = = $10^7 e^{-8.29l(Mn–L)}$ (r 0.99), respectively.

The comparison of the values of the equilibrium constants for the molecular complexes of zinc, aluminum [14, 15], and manganese 5,15-diphenyl-3,7,13,17-tetramethyl-2,8,12,18-tetrabutylporphyrinates shows that the stability of the latter is much lower due to the influence of the metal atom nature, *cis*,*trans*-effects and the deformation degree of the macrocycle (Fig. 1) on the coordination properties of the metal porphyrinates.

Based on the above it is possible to conclude that the coordinative unsaturation of the metal atom and its structure are effective ways of controlling the properties of manganese porphyrinates. The obtained results allow assessing the feasibility and effectiveness of the compound as an active component of the catalyst of various biological and technical processes.

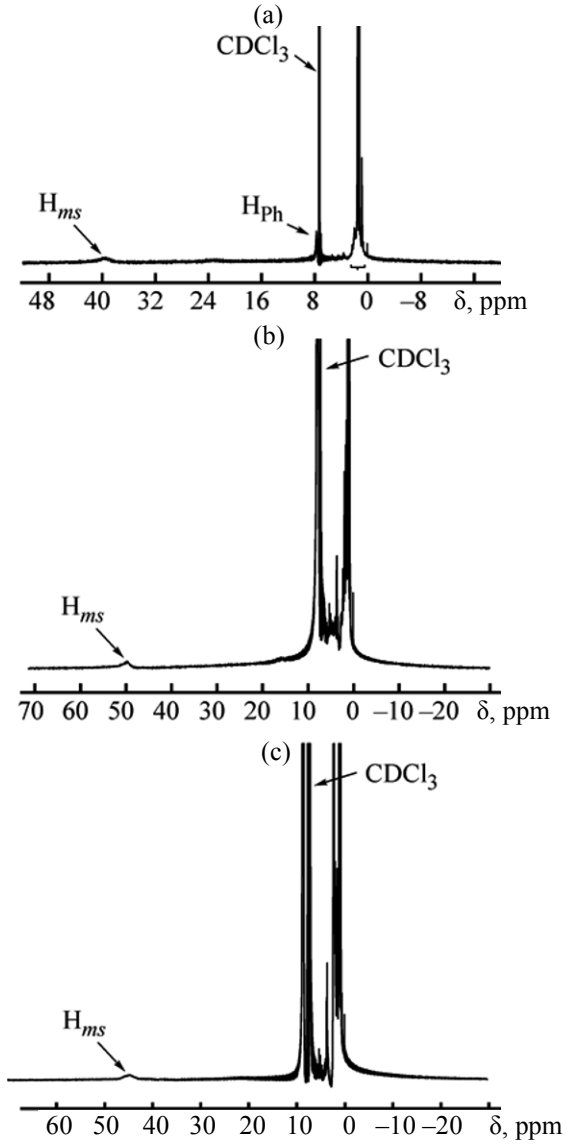


Fig. 5. The ^{1}H NMR spectra (a) of manganese porphyrinate and its molecular complexes with (b) imidazole and (c) pyridine.

EXPERIMENTAL

The electron absorption spectra were recorded on a Cary-50 spectrophotometer in the range of 380–700 nm. The optical density of a series of the working solutions of manganese(III) porphyrinate of constant concentration and solutions of the organic bases of different concentrations was measured at λ 368–480 nm in a cells (l 1). The temperature accuracy was less than 1 K. The relative error in determining the K_s values was 5–12%.

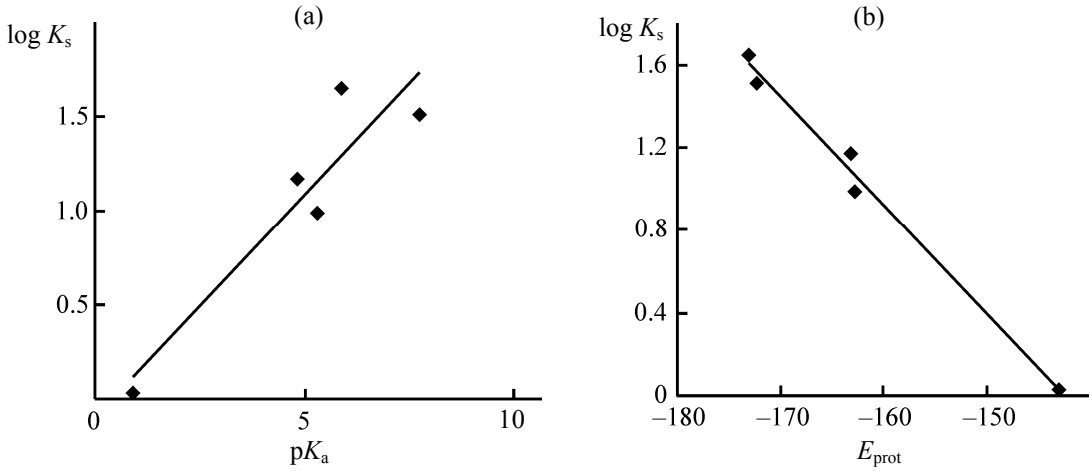


Fig. 6. The dependence of the stability of the molecular complexes (Ac)Mn(**L**)$_n$P on the (a) pK_a value and (b) the calculated energy of protonation of the organic bases (b).

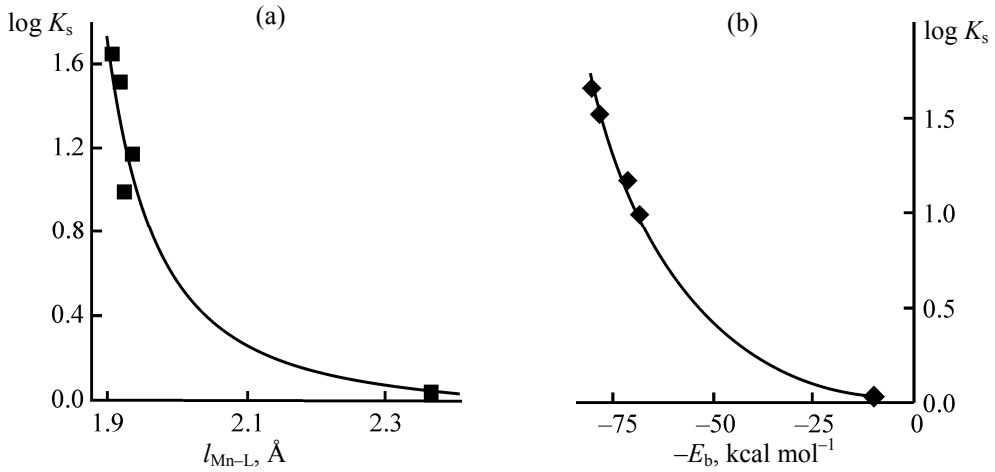


Fig. 7. The stability of the complexes (Ac)Mn(**L**)$_n$P vs (a) the Mn–L bond length and vs (b) its energy.

The equilibrium constant for the studied reaction was determined by the classical method [4, 5].

$$K_s = \{[(A_{mix} - A_0)/(A_\infty - A_{mix})]\cdot[(A_\infty - A_0)/(A_\infty - A_{mix})]\} \times 1/\{(c_L^0 - c_p^0)\cdot[(A_{mix} - A_0)/(A_\infty - A_{mix})]\}. \quad (1)$$

Table 2. The stability constants of the molecular complexes (Ac)Mn(**L**)P and the basicity parameters of extraligand

Complex	log $K_s^{298\ K}$	pK_a	$–E_{prot}$, kcal mol$^{–1}$
[MnP(Im)$_2$P](Ac)	3.53	6.65	169.36
(Ac)Mn(1-MeIm)P	1.51	7.33	172.27
(Ac)Mn(2-MeIm)P	1.65	5.89	173.06
(Ac)Mn(BiPy)P	1.17	4.82	163.06
(Ac)Mn(Py)P	0.99	5.29	162.79
(Ac)Mn(DMF)P	0.03	0.92	142.92

The quantum-chemical calculations were performed by the PM3 method [6–8] using the PC-version [17] of the GAMESS package [18]. The specified gradient of 0.0002 kJ mol$^{–1}$ Å$^{–1}$ was a condition for the account completing. The data preparation and processing were performed using ChemCraft 1.3 software [19]. The initial approximation was given based on the average structure of the metal porphyrinates [20]. The geometrical parameters for the alkyl substituents and organic bases correspond to the published data [21].

5,5-Diphenyl-3,7,13,17-tetramethyl-2,8,12,18-tetrabutylporphyrin was synthesized according to [16].

Manganese complex with 5,15-diphenyl-2,8,12,18-tetramethyl-3,7,13,17-tetrabutylporphyrin (Ac)MnP was synthesized via the reaction of porphyrin with 10-fold excess of manganese(III) acetate in acetonitrile at

reflux within 2–2.5 h; the reaction progress was monitored by the changes in the electron absorption spectrum of the reaction mixture. The reaction completeness was judged by the disappearance of the absorption bands of the porphyrin and an increase in the absorption bands of the manganese complex. Then acetonitrile was distilled off. The dry residue was dissolved in benzene. The benzene solution was washed with water and evaporated. The complex was chromatographed on a silica gel followed by recrystallization from methanol. Yield 80%, R_f 0.60 (benzene–ethanol, 30:1). UV spectrum, λ_{max}, nm (log ε): 368 (4.96), 479 (4.89), 572 (4.18). Found, %: C 75.45; H 7.50; N 6.50. $C_{54}H_{63}MnN_4O_2$. Calculated, %: C 75.85; H 7.43; Mn 6.43; N 6.55; O 3.74.

ACKNOWLEDGMENTS

This work was financially supported by the the Russian Academy of Sciences (Program for Basic Research "Theoretical and experimental study of the nature of chemical bonding and mechanisms of important chemical reactions and processes") and the Russian Foundation for Basic Research (grant nos. 12-03-00824-a, 11-03-00993-a).

REFERENCES

1. Koifman, O.I. and Ageeva, T.A., *Rus. Khim. Zh.,* 2004, vol. 48, no. 4, p. 140.
2. Nikolaeva, O.I., Kurek, S.S., Ageeva, T.A., and Koifman, O.I., *Izv. Vuzov, Ser. Khim. i Khim. Technol*., 2004, vol. 47, no. 2, p. 146.
3. Mamardashvili, N.Zh., Storonkina, O.E., and Mamardashvili, G.M., *Koord. Khim*., 2004, vol. 30, no. 6, p. 416.
4. Bulatov, M.I. and Kalinkin, I.P., *Prakticheskoe rukovodstvo po fotokolorimetricheskim i spektrofotometricheskim metodam analiza* (A Practical Guide to Photocolorimetric and Spectrophotometric Methods of Analysis), Khimiya, 1968, 183 p.
5. Zaitseva, S.S., Zdanovich, S.A., Semeikin, A.S., and Koifman, O.I., *Zh. Neorg. Khim.,* 2005, vol. 50, no. 11, p. 1919.
6. Stewart, J.J.P., *J. Comput. Chem*., 1989, vol. 10, no. 2, p. 221.
7. Fletcher, R., *Methods of Optimization*, New York: John Wiley & Sons, 1980, p. 45.
8. Stewart, J.J.P., *J. Computer-Aided Mol. Desing*, 1990, vol. 4, no. 1, p. 1.
9. *Tablitsy constant skorostei i ravnovesii gomoliticheskikh organicheskikh reaktsii* (Tables of Rate Constants and Equilibriums of Homolytic Organic Reactions), Izd. VINITI, 1976, vol. 2.
10. Reichardt, C., *Solvents and Medium Effects in Organic Chemistry*, Springer-Verlag, 1991.
11. Janson, T.R., Bouchern, L.J., and Katz, J.J., *Inorg. Chem*., 1973, vol. 12, no. 4, p. 940.
12. La Mar, G.N. and Walker, F.A., *J. Am. Chem. Soc*., 1973, vol. 95, no. 21, p. 6950.
13. La Mar, G.N. and Walker, F.A., *J. Am. Chem. Soc*., 1975, vol. 97, no. 18, p. 5103.
14. Zaitseva, S.V., Zdanovich, S.A., and Koifman, O.I., *Koord. Khim*., 2010, vol. 36, no. 5, p. 323.
15. Zaitseva, S.V., Zdanovich, S.A., and Koifman, O.I., *Proc. X Int. Conf. "Problems of Solvation and Complex Formation in Solutions,"* Suzdal, 2007, S-696.
16. Semeikin, A.S., Kuz'min, N.G., and Koifman, O.I., *Izv. Vuzov, Ser. Khim. i Khim. Technol*., 1988, vol. 31, no. 6, p. 39.
17. *http://classic.chem.msu.su/gran/gamess/index.html.*
18. Schmidt, M.W., Baldridge, K.K., Boatz, J.A., Elbert, S.T., Gordon, M.S., Jensen, J.H., Koseki, S., Matsonaga, N., Nguyen, KA, Su, S., Windus, T.L., Dupuis, M., and Montgomery, J.A., *J. Comput. Chem*., 1993, vol. 14, no. 11, p. 1347.
19. *http://www.chemcraftprog.com/index.html.*
20. *Porfiriny: struktura, svoistva, sintez* (Porphyrins: Structure, Properties, and Synthesis), Enikolopyan, N.S., Ed., Moscow: Nauka, 1985.
21. *Obshchaya organicheskaya khimiya,* Barton, D. and Ollis, W.D., Eds., Moscow: Khimiya, 1981, vols. 1, 2, 8.