Coordination Properties of Ga, In, and Tl Tetraphenylporphine Complexes in Reactions with Nitrogen-containing Extra Ligands

S. V. Zaitzeva, S. A. Zdanovich, T. A. Ageeva, and O. A. Golubchikov

Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, Russia Ivanovo State University of Chemical Engineering, Ivanovo, Russia

Received December 29, 2000

Abstract—The formation of Ga^{3+} , In^{3+} , and Tl^{3+} tetraphenylporphine mixed-ligand complexes (X)MTPP + L = (X)M(L)TPP (X = Cl⁻, AcO⁻, acac⁻; L = *N*-methylimidazole, imidazole, pyridine, 3,5-dimethylpyrazole, dimethylformamide) in chloroform was studied by spectrophotometric titration and quantum-chemical calculations. The stability of the Ga, In, and Tl porphyrin extra complexes was found to depend on the nature of the acido and nitrogen-containing ligands. The geometric and energetic characteristics of the complexes of six-coordinate gallium and indium porphyrins were calculated. Correlations between calculated and experimental energies of formation and Gibbs energies were found. The *cis-* and *trans*-effects of ligands in the extra complexes of metal porphyrins were explained.

Thermodynamic stability characteristics of metalporphyrin extra complexes are very important for interpretation of the physicochemical properties of these systems and for technological design. The interest in high-valent metal porphyrins is first of all connected with search for effective catalysts for redox processes [1–4]. The catalytic activity of such compounds is enhanced by their incorporation into extra complexes [3, 4]. This work is a continuation of a systematic study of the coordination properties of porphyrin complexes of aluminum-group metals and deals with special features of formation of mixedligand compounds of Ga, In, and Tl tetraphenylporphines in chloroform with various acido and extra ligands. Aluminum porphyrins were described earlier in [5, 6]. In the study we used spectrophotometric titration and computer simulation. The use of quantumchemical calculations for optimization of chemical processes and structures of various compounds was described in [7–9]. The dependence of the stability of extra complexes (X)M(L)TPP on the basicity of the molecular extra ligand L and the nature of the central metal atom and acido ligand X was characterized on the basis of calculated and experimental data. The geometric and energetic parameters of gallium, indium, and thallium porphyrins and of their extra complexes were calculated using the PM3 method.

Like with aluminum porphyrins, the formation of extra complexes with the compounds under produces significant changes in the positions and intensities of bands in the electronic absorption spectra (Fig. 1). This fact enables us to use the spectral method for studying the extra coordination which is described by the following equation.

(X)MTPP +
$$nL \iff (X)M(L)_nTPP$$
.

Metal porphyrin–extra ligand equilibrium is achieved almost immediately, which is experimentally proved by the corresponding electronic spectra (Fig. 1). Chloroform is a weak solvating agent for the central metal atoms of metal porphyrins, and, therefore, the effect of specific metal–CHCl₃ interactions on the equilibrium of extra coordination can be neglected.

The calculated stability constants (K_{st}) of the aluminum, gallium, and indium extra complexes (Table 1) show that the ability of metal porphyrin to coordinate extra ligand decreases from aluminum to thallium. First of all, this is attributable to the increasing ionic radius and ionization potential of the central atom [10]. The formation of the mixed-ligand compounds is also affected by the cis effect of ligands in the complex. In contrast to aluminum tetraphenylporphyn, M-X bonds in indium and thallium porphyrins seem to be stronger due to the fact that the latter metals have larger covalent radii and thus deviate significantly from the N⁴ plane. The geometric factor, too, contributes much into the ability of metal porphyrin to coordinate extra ligand. For instance, a much smaller size of gallium (r_{cov} 1.19 Å [10]) can give rise to radial deformation of the macroring in (X)GaTPP and thus decrease the covalent contribution



Fig. 1. Electronic absorption spectra of the mixed-ligand (Cl)GaTPP complex with imidazole (Im): (1) pure (Cl)GaTPP ($c_{(Cl)GaTPP} 9 \times 10^{-6}$ M); (2)–(10) (Cl)GaTPP with various imidazole concentrations ($c_{(Cl)GaTPP} 9 \times 10^{-6}$, $c_{Im} 6 \times 10^{-4}$ –9.4×10⁻³ M); and (11) (Cl)GaTPP with an excess of imidazole in chloroform.

into the Ga–N_p bond strength. Therewith, the Ga–X bond strengthens (Table 2). The deformation in the indium and thallium complexes { $r_{\rm cov}$ (In) 1.36 and $r_{\rm cov}$ (Tl) 1.45 Å [10]} and the resulting electron density redistribution of the macroring are not so

Table 1. Thermodynamic characteristics of imidazoleextra coordination to Al, Ga, and In porphyrins in chloro-form

Complex	$K_{\rm st} \times 10^{-3},$ l/mol (298 K)	–Δ <i>G</i> , kJ/mol	– <i>E</i> _b (M–N _L), kJ/mol	Δλ, nm
(Cl)AlTPP (AcO)AlTPP (Cl)GaTPP (AcO)GaTPP (Cl)InTPP (Cl)GaTPP ^b (AcO)GaTPP ^b (Cl)InTPP ^b	$\begin{array}{c} 4.0\pm 0.3^{a}\\ 12.0\pm 1.0^{a}\\ 1.88\pm 0.07\\ 2.9\pm 0.2\\ 0.135\pm 0.001\end{array}$	18.1 19.3 5.8	145.56 156.46 47.90 38.86 20.91 25.01	12.0 13.0 2.5

^a Data of [5, 6]; ^b metal porphyrins with imidazole in the *cis* position.

significant. This is probably responsible for the absence of correlation between stability and metalextra ligand $(M-N_L)$ bond length in the series of indium and gallium porphyrin extra complexes (Table 2). Thus, the data in Tables 1 and 2 suggest that the structural features of the compounds under study affect their coordination properties.

Compounds (X)AlTPP form complexes with *N*-methylimidazole (MeIm), imidazole (Im) pyridine (Py), 3,5-dimethylpyrazole (DMP), and dimethylformamide (DMF) [5, 6]. For (X)GaTPP and (Cl)InTPP only extra coordination with imidazole is typical, because this ligand is highly basic and produces no steric hindrances to $M-N_L$ bond formation. Using the Benth–French method [11], we found that gallium and indium tetraphenylporphine complexes coordinate one Im molecule each (Fig. 2).

Though MeIm is the strongest base among all the nitrogen-containing extra ligands under study, its coordination by gallium and indium porphyrins is almost impossible, which seems to be caused by the fact that the desolvation energy of *N*-methylimidazole in the case of chloroform, as calculated by the PM3 method [12], is double that of imidazole [5]. There-



Fig. 2. Dependences of log $[(A_e - A_0)/(A_{\infty} - A_0)]$ on log c_L for extra coordination of (1) (Cl)GaTPP, (2) (AcO)GaTPP, and (3) (Cl)InTPP with Im in chloroform.

fore, the formation of the (X)Ga(MeIm)TPP and (Cl)In(MeIm)TPP extra complexes becomes energetically unprofitable and the formation of M–MeIm bonds finds difficulties because of the energy consumption for desolvation. Steric distortions and spatial restrictions involved also prevent MeIm extra coordination. The complex (AcO)TITPP is not prone to extra cooordination with MeIm under the experimental conditions, since the increased ionic radius of the metal and the possibility of bidentate binding of AcO^- result in a stronger deviation of thallium from the macroring plane [13] and prevent *trans* addition of the molecular ligand to the acido ligand.

The ability of (AcO)M(L)TPP complexes to coordinate an extra molecule in the *cis* position is very weak, which is associated with steric hindrances arising from the neighborhood of two bulky ligands. The formation energies of the mixed-ligand compounds and the M-N_L bond strengths, obtained by quantum-chemical calculations (Tables 1 and 2), too, establish that extra ligands are most probably arranged on a side opposite to the acetate ion.

It should be noted that the ability of metal porphyrins to coordinate an extra ligand is strongly affected by the nature of the covalently bonded acido ligand X. Replacement of AcO⁻ by Cl⁻ in gallium tetraphenylporphyn complexes results in reduced stability of (Cl)Ga(Im)TPP, on account of the enhanced covalent nature of the Ga-Cl bond. Therefore, the reduction of the effective positive charge on the gallium atom results in destabilization of the extra complex. The strongest interaction between the metal and chlorine weakens the Ga-Im bond. Thus, in the systems under study the mutual trans effect of ligands in the extra complexes is very strong. The low stability of (AcO)M(Im)TPP complexes ($M = Ga^{3+}$, In^{3+}) results from both the steric strain in the porphyrin and the high polarizability of the elecronic shell of AcO⁻,

Table 2. Bond lengths (Å) in Ga and In porphyrin extra complexes

Complex	L	M-N ¹	M-N ²	M-N ³	M-N ⁴	M–X	M–N _L	MCt
(Cl)GaTPP		2.495	1.802	1.816	2.448	1.865		0.608
	Im	2.406	1.803	1.795	2.399	1.813	2.487	0.436
(AcO)GaTPP		1.802	1.793	2.361	2.399	2.218		0.478
	Im	1.800	1.794	2.335	2.352	2.283	2.380	0.287
(Cl)InTPP		2.089	2.091	2.088	2.077	2.528		0.329
	Im	2.088	2.090	2.085	2.075	2.651	2.124	0.066
(AcO)GaTPP ^a	Im	1.789	2.403	2.406	1.788	2.284	4.143	0.557
(Cl)GaTPP ^a	Im	2.486	1.794	1.794	2.458	1.809	3.482	0.710
(Cl)InTPP ^a	Im	2.076	2.094	2.077	2.093	2.592	3.978	0.329
		1	1			1		

^a Metal porphyrin with imidazole in the *cis* position.

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 73 No. 1 2003



Fig. 3. Structure of (Cl)In(Im)TPP calculated by the PM3 quantum-chemical method.

which substantially reduce the effective positive charge on the metal atom and the $M-N_L$ bond strength (Table 2).

As compared to porphyrin complexes of doublecharged metal ions [14–16], gallium and indium porphyrins form less stable extra complexes, even though their formal charge is higher. Obviously, there are several reasons for that. First, the X–M bond is covalent rather than ionic [17–20]. Second, the metal cation deviates from the N⁴ plane of the porphyrin to acido ligand X, which is proved by quantum-chemical calculations (Table 2). This deviation is also preserved in the extra complexes (Fig. 3).

Computer simulation based on quantum-chemical calculations allows us to predict the extra coordination process and to explain the trends in variation in the stability of the tetraphenylporphyrin extra complexes with acido and extra ligands. According to Table 1, the energy of $M-N_L$ bond formation (E_b) in the extra complexes changes in parallel with their stability.

The calculated changes in the geometry of metal porphyrins, produced by extra coordination, allow us to explain the specificity of this process for aluminum-subgroup metal complexes (Table 2). The mixed-ligand compounds have a square-pyramidal structure of the coordination centers, with the metal atoms deviating from the N^4 plane to the acido

ligands (Fig. 2). Since the macroring deformations are different in nature, no correlation between the stability of gallium and indium porphyrins and the deviation of the metal from the M-Ct plane is observed (Table 2). This type of deformation is preserved in extra complexes, but M-Ct distances decrease significantly. We have found no correlation between the macroring deformation (i.e. the size of the coordination cavity), Ct-M, M-X and M-Im, for the compounds under study. However, we found a dependence between $M-N_L$ bond strengths and K_{st} values for complexes of gallium porphyrins: As the $M-N_L$ bond length increases, the stability of the complexes decreases (Table 2). According to Table 2, when imidazole is coordinated by a metal porphyrin, the M-N_P bond is slightly strengthened but the M-X bond becomes longer. Thus, the trans effect is accompanied by the *cis* effect, which suggests the presence of a fairly strong mutual influence of ligands in the extra complexes.

EXPERIMENTAL

Spectrophotometric titration and computer simulation were used as investigation techniques. The experimental and calculation procedures were similar to those described in [6, 21]. Quantum-chemical calculations were carried out using the MOPAC 6.0 program. The geometry of aluminum porphyrins was optimized using a combination of conjugate gradient methods

Table 3. Metal–nitrogen $[v(M-N), cm^{-1}]$ and metal–acido ligand $[v(M-X), cm^{-1}]$ stretching vibrations frequencies in the IR spectra of (AcO)GaTPP, (Cl)InTPP, and (AcO)TITPP.

Complex	v(M–N)	v(M–X)
(AcO)GaTPP	450	573, 615 (Ga–O)
(Cl)InTPP	433	525, 566 (In–Cl)
(AcO)TITPP	430 [23]	562, 615 (Tl–O) [23]

of Fletcher–Reeves and Pollack–Ribiere [22]. The value 0.04 kJ mol⁻¹ Å⁻¹ for the gradient was accepted as a criterion for calculation termination. The experimental and calculated characteristics of the extra coordination process are shown in Tables 1 and 2.

Complexes (X)MTPP were obtained by reacting metal salts with tetraphenylporphine in a high-boiling solvent and isolated by liquid chromatography and recrystallization.

(AcO)GaTPP was obtained by the known procedure [7] by reacting H₂TPP and (AcO)Ga(OH) at a 1:2 molar ratio in boiling PhOH for 10 min. The reaction mixture was dissolved in chloroform and washed with warm water many times. The resulting solution of the complex in chloroform was dried by CaCl₂, concentrated, and subjected to chromatography on Al_aO₃ with chloroform as eluent. After repeated chromatography, the chloroform was distilled off in a vacuum. Yield 92%. Electronic absorption spectrum (CHCl₃), λ_{max} , nm (log ε): 627.2 (3.04), 587.5 (3.55), 547.0 (4.32), 512.0 sh, 418.2 (5.76).

(Cl)GaTPP was obtained by boiling (AcO)GaTPP in 33% HCl for 3 h. The acid was removed in a vacuum, the dry residue was dissolved in a small amount of CHCl₃, washed with water, dried with CaCl₂, subjected to chromatography on Al₂O₃ with chloroform as eluent. After repeated chromatography, the chloroform was distilled off in a vacuum. Yield 90%. Electronic absorption spectrum (CHCl₃), λ_{max} , nm (log ε): 620.0 (3.36), 581.0 (3.58), 545.0 (4.30), 510.0 sh, 416.4 (5.73).

(Cl)InTPP and (AcO)TITPP were synthesized by the procedure in [18, 19]. Electronic absorption spectrum for (Cl)InTPP (CHCl₃), λ_{max} , nm (log ε): 634.0 (3.19), 598.0 (3.83), 559.0 (4.39), 526.4 (3.55), 425.0 (5.85).

The metal porphyrins were identified by the characteristic vibration frequencies in the IR spectra recorded on an IKS-29 spectrophotometer in KBr pellets (Table 3). However, detailed interpretation of the spectra was beyond the scope of this work, and the spectral assignment was based on published data [23–25].

REFERENCES

- 1. Scheidt, W.R. and Lee, Y.J., *Struct. Bonding (Berlin)*, 1987, vol. 1, no. 1, p. 64.
- Kurori, M. and Inoue, S., J. Synth. Org. Chem. Jpn., 1989, vol. 47, no. 11, p. 1017.
- Wonwoo, N. and Selverston, V.J., J. Am. Chem. Soc., 1990, vol. 112, no. 12, p. 4977.
- 4. Arai, T. and Sato Y., Chem. Lett., 1990, no. 4, p. 551.
- 5. Zaitzeva, S.V., Cand. Sci. (Chem.) Dissertation, Ivanovo, 1999.
- Lomova, T.N., Zaitzeva, S.V., Molodkina, O.V., and Ageeva, T.A., *Koord. Khim.*, 1999, vol. 25, no. 6, p. 424.
- Stewart, J.J.P., J. Comput. Chem., 1989, vol. 10, no. 2, p. 209.
- Anderson, W.P., Edwards, W.D., and Zerner, M.C., *Inorg. Chem.*, 1986, vol. 25, no. 16, p. 2728.
- 9. Stewart, J.J.P., J. Computer-Aided Molecular Design, 1990, vol. 4, no. 1, p. 1.
- Batzanov, S.S., *Eksperimental'nye osnovy strukturnoi* khimii (Experimental Foundations of Structural Chemistry), Moscow: Izd. Standartov, 1986.
- Bulatov, M.I. and Kalinkin, I.P., Prakticheskoe rukovodstvo po fotokolorimericheskim i spektrofotometricheskim metodam analiza (Manual on Photocolorimetric and Spectrophotometric Analytical Methods), Leningrad: Khimiya, 1968.
- Stewart, J.J.P., J. Comput. Chem., 1991, vol. 12, no. 3, p. 320.
- 13. Collins, D.V. and Hoard, J.L., J. Am. Chem. Soc., 1970, vol. 92, no. 2, p. 3761.
- 14. Karmanova, T.V., Koifman, O.I., and Berezin, B.D., *Koord. Khim.*, 1983, vol. 9, no. 6, p. 772.
- 15. Koroleva, T.A., Koifman, O.I., and Berezin, B.D., *Koord. Khim.*, 1983, vol. 7, no. 8, p. 2007.
- Berezin, B.D., Uspekhi khimii porfirinov (Progress in Porphyrin Chemistry), St. Petersburg: NII Khimii St.-Peterb. Gos. Univ., 1997.
- 17. Lomova, T.N., Mozhzhukhina E.G., and Berezin, B.D., *Zh. Neorg. Khim.*, 1993, vol. 38, no. 9, p. 1552.
- Lomova, T.N., Mozhzhukhina E.G., and Shormanova, L.P., *Zh. Obshch. Khim.*, 1989, vol. 59, no. 10, p. 2317.

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 73 No. 1 2003

- 19. Lomova, T.N. and Mozhzhukhina, E.G., Zh. Neorg. Khim., 1997, vol. 42, no. 10, p. 1691.
- 20. Senge, M.O., Ruhlandt-Senge, K., and Kevin, J., J. Chem. Soc., Dalton Trans., 1993, no. 23, p. 3619.
- 21. Tipugina, M.Yu., Lomova, T.N., and Ageeva, T.A., *Zh. Obshch. Khim.*, 1999, vol. 69, no. 3, p. 459.
- 22. Fletcher R., Methods of Optimization, New York:

Wiley, 1980.

- 23. Cullen D.L., Meyer E.F., and Smith K.M., *Inorg. Chem.*, 1977, vol. 16, no. 5, p. 1179.
- 24. Henrick K., Matthews R., and Tasker P., *Inorg. Chem.*, 1977, vol. 16, no. 12, p. 3293.
- 25. Brady, F., Henrick, K., and Matthews, R., J. Organomet. Chem., 1981, vol. 210, no. 2, p. 281.