# Synthesis and study of organometallic complexes of octaphenyltetraazaporphyrinatoindium(III)

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Five-coordinate organometallic complexes RIn(TAPPh$_8$) (R = Ph, Bu) were synthesized by the reactions of chloro(octaphenyltetraazaporphyrinato)indium(III) ClIn(TAPPh$_8$) with organolithium and organomagnesium compounds. The optical, IR, and $^1$H NMR spectra of the complexes were studied. In the presence of pyridine, the photochemical insertion of CO$_2$ occurs at the In—C bond to form the carboxylate complexes (RCOO)In(TAPPh$_8$). A study of the kinetics of this reaction showed a higher stability of the In—C bond in the aryl PhIn(TAPPh$_8$) complex than that in the alkyl complex BuIn(TAPPh$_8$). The mechanism of the reaction was proposed.

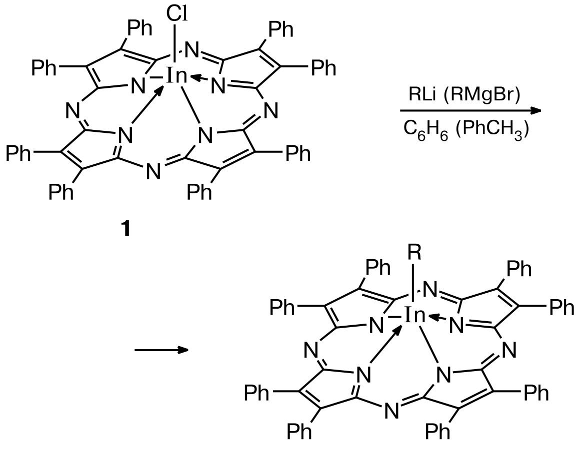
**Key words:** octaphenyltetraazaporphyrins, indium complexes, photochemical fixation, carbon dioxide.

Indium(III) complexes with porphyrin macrocycles are considered as promising materials with nonlinear optical properties.[1] The manifestation of such properties depends, to a great extent, on the nature of both macrocyclic and axial ligands. We have recently shown[2] for the iron(III) aryl complexes with octaphenyltetraazaporphyrin that the metal—carbon bond in organometallic porphyrin complexes with d-metals can be substantially stabilized by *meso*-tetraaza substitution. In order to elucidate the influence of aza substitution in porphyrins on the reactivity and stability of p-metal complexes, the phenyl and butyl derivatives of the indium(III) complex with octaphenyltetraazaporphyrin were synthesized and studied in this work.

## Results and Discussion

**Synthesis.** The reaction of the chloro(octaphenyltetraazaporphyrinato)indium(III) complex ClIn(TAPPh$_8$) (**1**) (TAPPh$_8$ is octaphenyltetraazaporphyrin) with organolithium and organomagnesium reagents (RLi, RMgBr) in anhydrous benzene or toluene, results in substitution of the Cl atom by the organic R group to form the RIn(TAPPh$_8$) complexes (R = Ph (**2a**), Bu (**2b**)) (Scheme 1).

**Scheme 1**



**1**

**2a,b**

R = Ph (**a**), Bu$^n$ (**b**)

Unlike organometallic derivatives of indium(III) porphyrinates,[3] which can be synthesized under anaerobic conditions only, tetraazaporphyrin derivatives are more stable toward oxygen and moisture and, therefore, they can be synthesized in both an inert atmosphere and air. The synthesis under aerobic conditions produces, along with the RIn(TAPPh$_8$) organometallic complexes, by-products, most likely, R-oxy and hydroxy derivatives, which are well separated by chromatography.

The structures of the products were confirmed by elemental analysis data and physicochemical methods (optical, IR, and $^1$H NMR spectroscopies).

**Spectral properties.** On going from the starting complex **1** to derivatives **2a** and **2b**, the main changes in the electronic absorption spectrum occur in the region of the B band ($a_{2u} \rightarrow \pi^*$ transition), whose bathochromic shift

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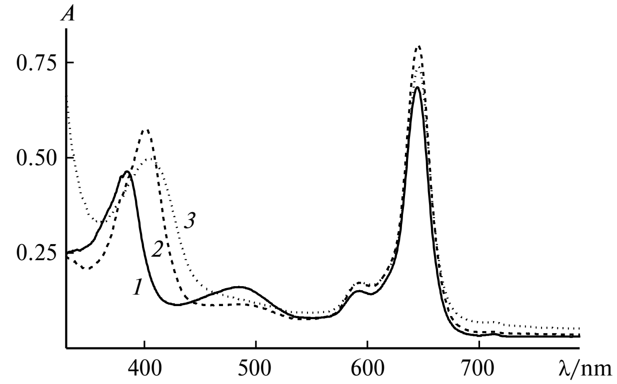


**Fig. 1.** Electronic absorption spectra of ClIn(TAPPh$_8$) (*1*), PhIn(TAPPh$_8$) (*2*), and BuIn(TAPPh$_8$) (*3*) in benzene.

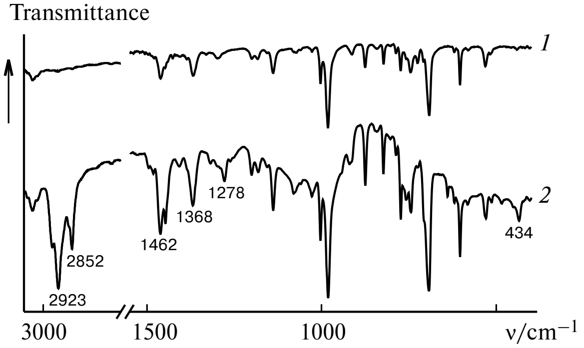


**Fig. 2.** IR spectra of ClIn(TAPPh$_8$) (*1*) and BuIn(TAPPh$_8$) (*2*) (pellets with KBr).

is 17 and 22 nm, respectively (Fig. 1 and Table 1). The position of the Q band ($a_{1u} \rightarrow \pi^*$ transition) remains virtually unchanged due to the fact that the $a_{1u}$ orbital, unlike $a_{2u}$, is less sensitive to changes in the coordination sphere of the In atom because the former orbital has zero coefficients at the coordinated pyrrole N atoms.[4] The coordination of the organic ligand in the axial position results in filling of the $p_z$ orbital of the In$^{III}$ atom. This orbital interacts with the $a_{2u}$ orbital of the macrocyclic ligand and destabilizes it, resulting in the bathochromic shift of the B band. The bathochromic shift observed for complex **2b** is greater than that for **2a** because the Bu group is a stronger σ-donor than the Ph group. When the Cl$^-$ anion is replaced by the organic ligand with stronger σ-donating properties, the intensity of the band at 485 nm in the electronic absorption spectrum also decreases. This band corresponds to the transfer of a charge from the nonbonding orbitals of the *meso*-N atoms to the π-antibonding orbitals of the macrocyclic ligand ($n \rightarrow \pi^*$ transition).[5]

**Table 1.** Parameters of the electronic absorption spectra of the indium(III) complexes with octaphenyltetraazaporphyrin in benzene

| Compound | λ/nm (logε) | | | |
|---|---|---|---|---|
| | B | Q´ | Q | CT* |
| ClIn(TAPPh$_8$) (**1**) | 384<br>(4.62) | 593<br>(4.12) | 645<br>(4.73) | 485<br>(4.17) |
| PhIn(TAPPh$_8$) (**2a**) | 401<br>(5.23) | 593<br>(4.58) | 645<br>(5.24) | — |
| BuIn(TAPPh$_8$) (**2b**) | 406<br>(4.49) | 594<br>(4.07) | 645<br>(4.69) | — |
| (PhCO$_2$)In(TAPPh$_8$) (**3a**) | 378<br>(4.88) | 592<br>(4.23) | 644<br>(4.93) | 484<br>(4.23) |
| (BuCO$_2$)In(TAPPh$_8$) (**3b**) | 377 | 594 | 645 | 470 |

* Charge transfer.

In the IR spectra the most informative for the identification of the complexes is the low-frequency region (100—500 cm$^{-1}$) containing bands corresponding to deformation vibrations of the In—C bond: 442 and 434 cm$^{-1}$ for complexes **2a** and **2b**, respectively (Figs. 2 and 3). The spectrum of complex **2a** (see Fig. 3) also exhibits a band from the stretching vibration of the In—C bond at 251 cm$^{-1}$. In the region of medium frequencies (400—2000 cm$^{-1}$), vibrations of the coordinated Ph and Bu ligands are disguised by more intense vibrations of the tetraazaporphyrin macrocycle.[5,6] This is especially characteristic of complex **2a**, whose the spectral bands of the axial Ph group coincide with those of eight equatorial Ph rings. In the IR spectrum of complex **2b**, the bands of stretching vibrations of the Bu group are disguised by intense bands of skeletal vibrations of the macrocycle in regions of 1450—1460 and 1370—1380 cm$^{-1}$ (see Fig. 2). However, the IR spectrum contains a band with a medium intensity at 1278 cm$^{-1}$, which can likely be assigned to vibrations of the C—C bonds of the alkyl group.[7] The presence of the Bu group is reliably indicated by the presence of stretching vibrations of the C—H bonds in a high-frequency region of 2850—2950 cm$^{-1}$ in the IR spectrum of complex **2b**. These vibrations are characteristic of al-

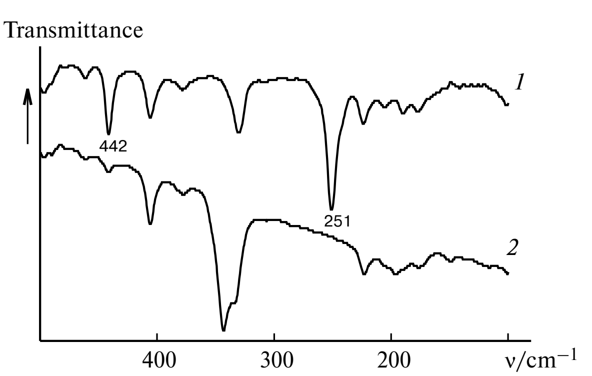


**Fig. 3.** Low-frequency IR spectra of PhIn(TAPPh$_8$) (*1*) and ClIn(TAPPh$_8$) (*2*) (molded in polyethylene).

**Table 2.** Parameters of the $^1$H NMR spectra of the indium(III) complexes with octaphenyltetraazaporphyrin

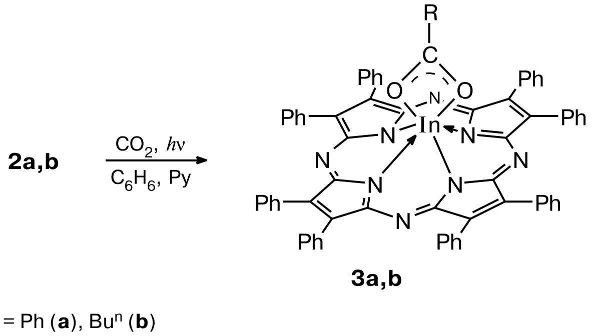
| Compound | δ | | | | | | |
|---|---|---|---|---|---|---|---|
| | Protons of β-substituents | | | Protons of axial group | | | |
| | *o*-Ph | *m*-Ph | *p*-Ph | *o*-Ph | *m*-Ph | *p*-Ph | |
| ClIn(TAPPh$_8$) (**1**)[5] | 8.32 | 7.62 | 7.64 | — | — | — | |
| PhIn(TAPPh$_8$) (**2a**) | 8.32 | 7.62 | 7.57 | 4.10 | 6.06 | 6.32 | |
| (PhCO$_2$)In(TAPPh$_8$) (**3a**) | 8.34 | 7.63 | 7.61 | 6.54 | 6.75 | 7.01 | |
| (PhO)In(TAPPh$_8$) (**4**) | 8.00 | 7.53 | 7.44 | | Not found | | |
| PhIn(PEt$_8$)[3] | — | — | — | 2.71 | 5.51 | 5.84 | |
| | | | | α-H | β-H | γ-H | δ-H |
| BuIn(TAPPh$_8$) (**2b**) | 8.31 | 7.61 | 7.57 | −2.94 | −1.36 | −0.93 | −0.12 |
| BuIn(PEt$_8$)[3] | — | — | — | −4.64 | −2.60 | −1.60 | −0.61 |

kanes.[8] The IR spectra of the In$^{III}$ complexes with octaphenyltetraazaporphyrin exhibit a characteristic band at 1280—1300 cm$^{-1}$. It is typical of the complexes with the $C_{4v}$ symmetry, for example, the five-coordinate Fe$^{III}$ complexes[6] in which the metal atom also deviates considerably from the macrocycle plane.

In the $^1$H NMR spectra of complexes **2a** and **2b**, signals from the protons of the equatorial Ph rings lie in the same region as those of **1**,[5] namely, as a doublet at δ 8.32 for the *ortho*-protons and as a multiplet at δ 7.57—7.62 for the *meta*- and *para*-protons. The strong π-ring current in the tetraazaporphyrin system results in shielding of the protons of the axial groups, and the protons nearest to the macrocycle undergo the greatest shielding. The signals from the *ortho*-protons of the Ph group lie at δ 4.10, and those from the protons of the α-CH$_2$ fragment of the Bu group lie at δ −2.94 (Table 2). At the same time, the protons of the axial groups in complexes **2a** and **2b** are less shielded than those of the In$^{III}$ complexes with porphyrins.[3] The signals from the *ortho*-protons of the Ph group exhibit the downfield shift by 1.39 ppm, and the signals from the protons of the α-CH$_2$ fragment of the Bu group are shifted by 1.7 ppm compared to those of similar In$^{III}$ complexes with porphyrins. This points to a greater deviation of the In atom from the macrocycle plane in tetraazaporphyrins compared to porphyrins induced by a decrease in the size of the coordination cavity upon *meso*-tetraaza substitution.[9] We have previously[10] shown that this results in a decrease in the bond strength of the In atom with coordinated atoms of the macrocycle upon *meso*-aza substitution. At the same time, the In$^{III}$ complexes with octaphenyltetraazaporphyrins exhibit a higher stability of the In—C bond with the axial organic ligand. This fact can be explained by the fact that a decrease in the coordination sphere upon aza substitution and a simultaneous enhancement of the π-withdrawing properties of the macrocyclic ligand favor the conjugation of the 5p$_z$ orbital of the In atom with the π-system of the macrocycle. As a result, electrons occupying the 5p$_z$ orbital of the In atom through σ-bonding with the organic ligand are efficiently delocalized over the conjugated π-system of the macrocycle to enhance the withdrawing properties of the In atom and to strengthen the In—C bond upon aza substitution. The previous study of the In$^{III}$ complexes with octaethyl- and tetraphenylporphyrins containing organic ligands with different σ-donating properties has shown[11] that the stability of the In—C bond is determined by the interaction of the 5p$_z$ orbital of the In atom with the porphyrin π-system.

**Reaction with CO$_2$.** Insertion of the CO$_2$ molecule at the In—C bond is an interesting property found[12] for the indium(III) porphyrinate complexes with organic ligands. The study of the reactions of complexes **2a** and **2b** with CO$_2$ in benzene allowed us to establish that, similarly to the In complexes with porphyrins,[12] the necessary condition for this reaction to occur (Scheme 2) is the presence of pyridine and irradiation of the solution with the visible light.

**Scheme 2**



R = Ph (**a**), Bu$^n$ (**b**)

Compound **3a**, which was isolated from a solution of complex **2a** in a benzene—pyridine (3 : 1) mixture after CO$_2$ was passed through the solution under visible light irradiation (see Experimental, method *A*), is identical to the benzoate complex (PhCOO)In(TAPPh$_8$) obtained by the independent synthesis from the HalIn(TAPPh$_8$) halide complex (Hal = Cl, Br) and tetra(*n*-butyl)ammonium benzoate (method *B*).

On transforming complexes **2a** and **2b** into carboxylate derivatives **3a** and **3b**, the main changes in the electronic absorption spectra are observed in the UV region: the position of the Q band remains almost unchanged, and the maximum of the B band undergoes the hypsochromic shift by 23 and 29 nm for **3a** and **3b**, respectively. In addition, the band of the $n \to \pi^*$ transition appears at 484 and 470 nm, respectively. The electronic absorption spectrum resembles the spectrum of the chloride complex **1**.[5] Complex **3a** was isolated and characterized by IR and $^1$H NMR spectroscopies.

The IR spectra manifest vibrations of the carboxylate group, and positions of the bands from symmetric and antisymmetric stretching vibrations of the COO group suggest the coordination of the carboxylate by the In atom. For example, in the IR spectrum of complex **3a** these vibrations appear at 1497 and 1447 cm$^{-1}$. The difference $\Delta\nu$ = 50 cm$^{-1}$ is characteristic of the bidentate coordination ($\Delta\nu$ = 40—80 cm$^{-1}$), whereas this value is much greater for monodentate coordination ($\Delta\nu$ = 220—320 cm$^{-1}$).[13]

In the $^1$H NMR spectrum of the benzoate complex **3a**, the signals from the axial Ph group exhibit a downfield shift compared to those from the phenyl derivatives **2a**. They appear at δ 6.54 (*o*-Ph$_{ax}$), 6.75 (*m*-Ph$_{ax}$), and 7.01 (*p*-Ph$_{ax}$) (see Table 2), indicating a decrease in the shielding influence of the porphyrin system on the protons of the Ph group because the latter is more remote from the macrocycle plane in complex **3a** than in **2a**. The positions of signals from the protons of the equatorial Ph groups in the $^1$H NMR spectrum of **3a** remain almost unchanged compared to those of the phenyl or chloride complexes **2a** and **1** (see Table 2). In our opinion, this also favors the bidentate coordination of the benzoate. For monodentate bonding, the deviation of the Ph ring from the normal to the mean plane of the macrocycle should change the shielding of the peripheral Ph groups, as it is observed, *e.g.*, for (PhO)In(TAPPh$_8$) (**4**). In the latter case, the signals from the protons of the equatorial Ph groups exhibit a substantial upfield shift and appear at δ 8.00 (*o*-Ph$_\beta$), 7.53 (*m*-Ph$_\beta$), and 7.44 (*p*-Ph$_\beta$) (see Fig. 2).

We studied the kinetics of insertion of the CO$_2$ molecule at the σ-In—C bond in RIn(TAPPh$_8$) using the spectrophotometric method. It was established in blank experiments that (a) addition of pyridine to a benzene solution of RIn(TAPPh$_8$) does not remarkably change the electronic absorption spectra, (b) these solutions are stable under visible light irradiation within the time of experiment, (c) no spectral changes are observed when CO$_2$ is passed through the solutions under dark conditions, (d) electronic absorption spectrum of a benzene solution of RIn(TAPPh$_8$) in the absence of pyridine remains unchanged under visible light irradiation and simultaneous passing CO$_2$. Changes in the electronic absorption spectrum, indicating the formation of the (RCOO)In(TAPPh$_8$) carboxylate complex, are detected only when CO$_2$ is passed through a benzene solution of RIn(TAPPh$_8$) in the presence of pyridine under visible light irradiation. The pattern of the spectral changes in the region of the B band is presented in Fig. 4 (changes in the region of the Q band are insignificant).

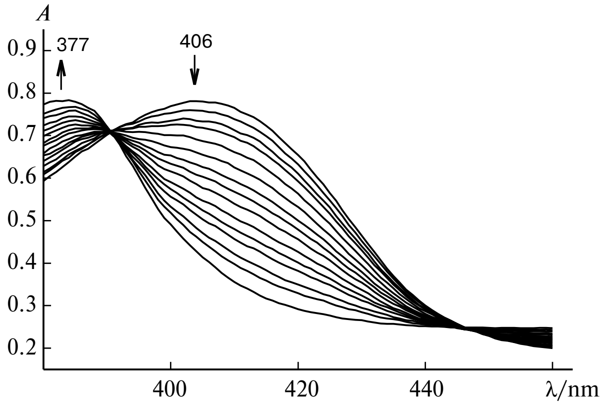


**Fig. 4.** Changes in the electronic absorption spectra induced by the reaction of BuIn(TAPPh$_8$) with CO$_2$.

The linear plot of ln($C_0/C$) for complex **2b** *vs.* irradiation time (Fig. 5) points to the first order of the reaction with respect to the concentration of complex **2b**. The values obtained for the apparent rate constants $k_{app}$ are presented in Table 3. On going from the butyl to phenyl derivatives under comparable conditions, the reaction rate 20-fold decreases. The photochemical character of the formation of the carboxylate complexes assumes that its rate should be determined first of all by the stability of the In—C bond toward homolytic cleavage. The kinetic data obtained suggest a greater stability of the In—Ph bond compared to the In—Bu bond. This agrees with the IR

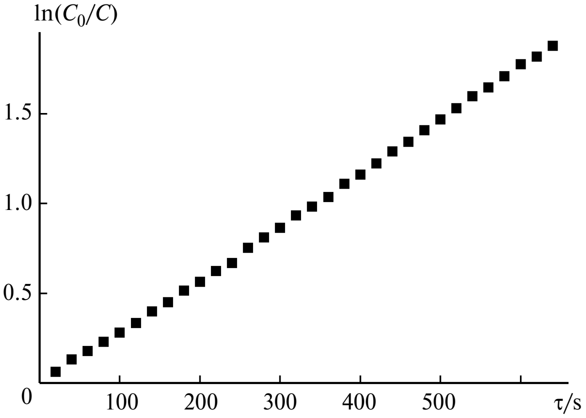


**Fig. 5.** Plot of ln($C_0/C$) *vs.* irradiation time (τ) for the photochemical reaction of BuIn(TAPPh$_8$) (**2b**) with CO$_2$.

**Table 3.** Apparent reaction rate constants ($k_{\mathrm{app}}$) of the photochemical insertion of $CO_2$ at the In—C bond at 298 K and their dependence on the pyridine concentration

| Compound | $C_{\mathrm{Py}}$/mol L$^{-1}$ | log($C_{\mathrm{Py}}$/mol L$^{-1}$) | $k_{\mathrm{app}}$/s$^{-1}$ | −log($k_{\mathrm{app}}$/s$^{-1}$) |
|---|---|---|---|---|
| PhIn(TAPPh$_8$) (**2a**) | 3.091 | 0.490 | 0.000139±0.000008 | 3.86 |
| BuIn(TAPPh$_8$) (**2b**) | 3.091 | 0.490 | 0.00282±0.00013 | 2.55 |
| | 4.945 | 0.694 | 0.00476±0.00029 | 2.34 |
| | 6.182 | 0.791 | 0.00524±0.00021 | 2.28 |
| | 9.273 | 0.967 | 0.00926±0.00055 | 2.03 |
| | 11.746 | 1.069 | 0.0125±0.00059 | 1.90 |

spectroscopic data, which show that the stretching vibrations of the In—Ph bond have a higher frequency than those of the In—Bu bond (442 and 434 cm$^{-1}$, respectively). Since the σ-donating properties of the Bu group are more pronounced than those of the Ph group, we can assume for the latter an additional effect of π-back bonding π*(Ph) ← $d_\pi$(In) due to the overlap of the $4d_\pi$ orbitals of the In atom with the vacant antibonding π* orbitals of the benzene ring.

We also attempted to elucidate the role of pyridine in the reaction. The invariabling of the spectra of **2a** and **2b** in the presence of pyridine indicates, in our opinion, that the pyridine molecule does not coordinate to the In atom. As found previously,[14] bases like pyridine do not either coordinate to the In porphyrin complexes. At the same time, our data for the insertion of $CO_2$ to the In—C bond in molecule **2b** (see Table 3) showed that an increase in the carboxylation rate is proportional to the pyridine concentration. The plot of log$k_{\mathrm{app}}$ *vs*. log($C_{\mathrm{Py}}$) is linear, and its slope is close to unity ($r$ = 0.994, tgα = 1.1) (Fig. 6). This points to the formation of an intermediate containing one pyridine molecule. It can be assumed that this intermediate is a donor-acceptor complex of pyridine with $CO_2$. The formation of the Py•$CO_2$ adduct in a pyridine solution of $CO_2$ has been found[15] by IR spectroscopy. The donor-acceptor interaction of $CO_2$ with pyridine increases the nucleophilicity of the $CO_2$ molecule, and the Py•$CO_2$ adduct is coordinated at the *cis*-position to the In atom. The In$^{\mathrm{III}}$ complexes with macrocyclic ligands, *e.g.*, phthalocyanines,[16—18] are characterized by similar *cis*-coordination of oxygen-containing ligands (RCOO$^-$, $CO_3{}^{2-}$, $NO_2{}^-$). Visible light irradiation favors the homolytic cleavage of the In—C bond accompanied by the rearrangement resulting in the formation of the carboxylate complex (Scheme 3). This mechanism differs from that proposed[12] for the In$^{\mathrm{III}}$ complexes with porphyrins, according to which the pyridine molecule coordinates at the *trans*-position to the R group. In the case of *trans*-coordination the In atom should be located in the macrocycle plane, which seems improbable, especially for the In complexes with tetraazaporphyrins. It is known[9] that *meso*-tetraaza substitution substantially decreases the size of the coordination cavity of the porphyrin macrocycle. In addition, the formation of porphyrin complexes with the *trans*-configuration is usually characteristic[19] of metals with the ion radius $r_{\mathrm{M}}$ < 0.7 Å, while $r_{\mathrm{In}}$ = 0.81 Å.[20]

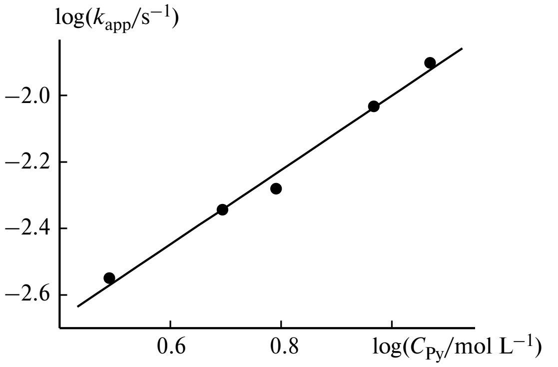
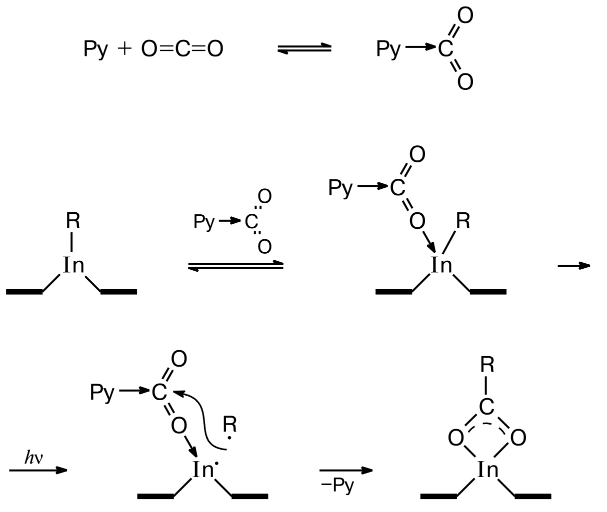


**Fig. 6.** Logarithmic plot of the apparent rate constant ($k_{\mathrm{app}}$) of the photochemical reaction of BuIn(TAPPh$_8$) (**2b**) with $CO_2$ *vs*. the pyridine concentration ($C_{\mathrm{Py}}$).

**Scheme 3**



Thus, this study confirmed the stabilization of the metal—carbon bond in the porphyrin complexes by tetraaza substitution, which can be significant in their practical use.

## Experimental

The syntheses of complexes **2a,b** were based on a procedure proposed[3] for the preparation of the organometallic $In^{III}$ complexes with porphyrins. The starting chloride complex **1** was synthesized using a known procedure.[5] Butyl lithium, tetrabutylammonium (Fluka), and phenyl lithium (Merck) were used. Benzene, toluene, and tetrahydrofuran were dried by distillation above metallic sodium, Py was distilled above KOH, and CaO and Mg chips were used for the distillation of $CH_2Cl_2$ and MeOH, respectively.

Electronic absorption spectra of solutions of the studied compounds ($1 \cdot 10^{-6}$—$1 \cdot 10^{-5}$ mol $L^{-1}$) were recorded on a Hitachi U-2000 spectrophotometer in the interval from 200 to 1000 nm. IR spectra were recorded on NIC 5DXB (400—4000 $cm^{-1}$, pellets with KBr) and Bruker IFS 66 CS (80—500 $cm^{-1}$, pressings in polyethylene) FTIR spectrometers. $^1H$ NMR spectra were obtained on a Brucker AM 400 (400 MHz) spectrometer in $CD_2Cl_2$ at 293 K.

**σ-Phenyl(2,3,7,8,12,13,17,18-octaphenyltetraazaporphyrinato)indium(III) (2a).** Phenyl lithium (0.02 mmol, a 20% solution in a $C_6H_{12}$—$Et_2O$ (7 : 3) mixture) was added with stirring to a solution of compound **1** in thoroughly dehydrated benzene or toluene (10 mL). After filtration, the solution was chromatographed on $Al_2O_3$ using benzene as eluent. The solvent from the first fraction containing complex **2a** was removed on a rotary evaporator. The yield was 8.7 mg (40%). Found (%): C, 75.33; H, 4.25; N, 9.80. $C_{70}H_{45}InN_8$. Calculated (%): C, 75.54; H, 4.08; N, 10.07. EAS (benzene), $\lambda_{max}$/nm (logε): 401 (5.23), 593 (4.58), 645 (5.24). $^1H$ NMR, δ: 8.32 (d, 16 H, *o*-$Ph_\beta$, $J$ = 8 Hz); 7.62 (m, 16 H, *m*-$Ph_\beta$); 7.57 (m, 8 H, *p*-$Ph_\beta$); 4.10 (d, 2 H, *o*-$Ph_{ax}$, $J$ = 8 Hz); 6.06 (t, 2 H, *m*-$Ph_{ax}$, $J$ = 8 Hz); 6.32 (s, 1 H, *p*-$Ph_{ax}$). IR, ν/$cm^{-1}$: 251 w (δ(In—C)); 442 m (ν(In—C)); 531 m, 604 m, 691 v.s, 745 m, 773 m, 822 m, 875 m, 982 v.s, 1003 m, 1080 w, 1182 w, 1139 m, 1199 w, 1298 m, 1367 m, 1461 m, 3055 cp.

**σ-Butyl(2,3,7,8,12,13,17,18-octaphenyltetraazaporphyrinato)indium(III) (2b)** was synthesized according to a similar procedure using BuLi (a solution in *n*-hexane, 1.6 mol $L^{-1}$) in 27% yield (5.4 mg). Found (%): C, 73.85; H, 4.78; N, 9.62. $C_{68}H_{49}InN_8$. Calculated (%): C, 74.72; H, 4.52; N, 10.25. EAS (benzene), $\lambda_{max}$/nm (logε): 406 (4.49), 594 (4.07), 645 (4.69). $^1H$ NMR, δ: 8.31 (d, 16 H, *o*-$Ph_\beta$, $J$ = 7 Hz); 7.61 (m, 16 H, *m*-$Ph_\beta$); 7.57 (m, 8 H, *p*-$Ph_\beta$); –0.12 (t, 3 H, $CH_2CH_2CH_2C\underline{H}_3$, $J$ = 7 Hz); –0.93 (m, 2 H, $CH_2CH_2C\underline{H}_2CH_3$); –1.36 (m, 2 H, $CH_2C\underline{H}_2CH_2CH_3$); –2.94 (t, 2 H, $C\underline{H}_2CH_2CH_2CH_3$, $J$ = 7 Hz). IR, ν/$cm^{-1}$: 434 m (ν(In—C)), 529 m, 604 s, 639 w, 692 v.s, 743 m, 773 m, 822 m, 875 m, 982 v.s, 1003 s, 1080 m, 1139 m, 1182 w, 1200 w, 1278 m (ν(C—C)$_{Bu}$); 1368 m, 1408 w, 1446 m, 1462 s, 2852 m (ν(CH)$_{Bu}$); 2923 s (ν(CH)$_{Bu}$).

**Benzoato(2,3,7,8,12,13,17,18-octaphenyltetraazaporphyrinato)indium(III) (3a).** ***A.*** Carbon dioxide was passed for 1 h through a solution of complex **2a** (10 mg, 0.009 mmol) in a Py—$C_6H_6$ (1 : 3) mixture under irradiation with a halogen lamp (75 W) mounted 20—25 cm from the reaction flask. After the end of the reaction (spectrophotometric monitoring), the reaction mixture was chromatographed on $Al_2O_3$ using $C_6H_6$ as eluent. After the solvent was removed, the yield of the product was 8.8 mg (85%).

***B.*** A 25% solution (0.5 mL) of tetrabutylammonium hydroxide in MeOH was added to a solution of benzoic acid (50 mg, 0.41 mmol) in THF (20 mL), and then BrIn(TAPPh$_8$) (50 mg. 0.044 mmol) was added. The mixture was refluxed for 3 h. After cooling, the reaction mixture was diluted with MeOH (40 mL). The black-violet precipitate that formed was filtered off and washed with MeOH. The substance obtained was chromatographed on $Al_2O_3$ using $CH_2Cl_2$ as eluent. After the solvent was removed, the yield of the product was 37 mg (~70%). Found (%): C, 73.55; H, 4.27; N, 9.38. $C_{71}H_{45}InN_8O_2$. Calculated (%): C, 73.71; H, 3.92; N, 9.68. EAS ($C_6H_6$), $\lambda_{max}$/nm (logε): 378 (4.88), 484 (4.23), 592 (4.23), 644 (4.93). IR, ν/$cm^{-1}$: 534 m, 604 m, 692 s, 745 m, 775 m, 787 w, 822 m, 875 w, 914 w, 983 v.s, 1003 m, 1027 w, 1140 m, 1183 w, 1200 w, 1301 m, 1368 m, 1385 s, 1447 w (ν(C—O)); 1460 w, 1497 m (ν(C—O)); 1602 m. $^1H$ NMR, δ: 8.34 (d, 16 H, *o*-$Ph_\beta$, $J$ = 8 Hz); 7.63 (m, 16 H, *m*-$Ph_\beta$); 7.61 (m, 8 H, *p*-$Ph_\beta$); 6.54 (d, 2 H, *o*-$Ph_{ax}$, $J$ = 9 Hz); 6.75 (t, 2 H, *m*-$Ph_{ax}$, $J$ = 7 Hz); 7.01 (t, 1 H, *p*-$Ph_{ax}$, $J$ = 7 Hz).

**Phenoxo(2,3,7,8,12,13,17,18-octaphenyltetraazaporphyrinato)indium(III) (4).** A 25% solution (0.25 mL) of tetrabutylammonium hydroxide in MeOH was added to a solution of PhOH (21 mg, 0.22 mmol) in THF (20 mL), and then BrIn(TAPPh$_8$) (50 mg, 0.044 mmol) was added. The mixture was refluxed for 1 h. After cooling, the reaction mixture was mixed with water (40 mL). The crystalline precipitate that formed was filtered off, washed with water and MeOH, and chromatographed on $Al_2O_3$ using $CH_2Cl_2$ as eluent. After the solvent was removed, the yield of complex **4** was 35 mg (~70%). Found (%): C, 74.38; H, 4.35; N, 9.71. $C_{70}H_{45}InN_8O$. Calculated (%): C, 74.47; H, 4.02; N, 9.93. EAS ($C_6H_6$), $\lambda_{max}$/nm ($I_{rel}$): 474 (0.24), 592 (0.22), 644 (1). IR, ν/$cm^{-1}$: 517 w, 532 m, 579 w, 604 s, 620 w, 692 v.s, 745 m, 757 m, 774 m, 787 w, 822 m, 840 w, 875 m, 915 m, 981 v.s, 1003 s, 1027 w, 1072 w, 1140 m, 1183 w, 1200 w, 1300 w, 1367 m, 1447 m, 1462 m, 1574 w, 1600 m. $^1H$ NMR, δ: 8.00 (d, 2 H, *o*-$Ph_\beta$, $J$ = 7 Hz); 7.53 (t, 2 H, *m*-$Ph_\beta$, $J$ = 7 Hz); 7.44 (t, 1 H, *p*-$Ph_\beta$, $J$ = 7 Hz).

**Kinetics.** Solutions of RIn(TAPPh$_8$) ($0.85$—$2.80 \cdot 10^{-5}$ mol $L^{-1}$) in a $C_6H_6$—Py mixture, in which the pyridine concentration was varied within 3.09—11.75 mol $L^{-1}$, were used to study the kinetics of the photochemical insertion of $CO_2$ at the In—C bond. The solution was placed in a spectrophotometric cell, whose temperature was maintained at 298 K, and was saturated with $CO_2$ in the dark for 20 min and then was periodically irradiated with a halogen lamp (75 W) mounted on the spectrophotometer at a distance of 20 cm from the cell. After each irradiation cycle, electronic absorption spectra of the solution were recorded in the wavelength interval from 380 to 480 nm.

Kinetic runs were carried out under the conditions of a reaction of the pseudo-first order, *i.e.*, with a great $CO_2$ excess over complexes **2a,b**. The apparent reaction rate constant ($k_{app}$) was calculated by the equation

$$k_{app} = (1/\tau)\ln[(A_\infty - A_0)/(A_\infty - A_\tau)],$$

where τ is the irradiation time, s; $A_0$, $A_\infty$, and $A_\tau$ are the initial, final, and current absorbances at the analytical wavelength (406 and 410 nm for complexes **2a** and **2b**, respectively).

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## References

1. M. Hanack and H. Heckman, *Eur. J. Inorg. Chem.*, 1998, **1**, 367.
2. P. A. Stuzhin, O. V. Mal´chugina, S. Wolowiec, L. Latos-Grazynzki, and B. D. Berezin, *Mendeleev Commun.*, 1998, 143.
3. P. Cocolios, R. Guilard, and P. Fournari, *J. Organomet. Chem.*, 1979, **179**, 311.
4. S. S. Dvonikov, V. N. Knyukshto, V. A. Kuzmitsky, A. M. Shulga, and K. N. Solovyov, *J. Luminescence*, 1981, **23**, 373.
5. P. A. Stuzhin, I. S. Migalova, and Kh. Khomborg, *Koord. Khim.*, 2000, **26**, 9 [*Russ. J. Coord. Chem.*, 2000, **26** (Engl. Transl.)].
6. P. A. Stuzhin, M. Hamdush, and U. Ziener, *Inorg. Chim. Acta*, 1995, **236**, 131.
7. K. N. Colov´ev, L. L. Gladkov, A. S. Starukhin, and S. F. Shkirman, *Spektroskopiya porfirinov: kolebatel´nye sostoyaniya* [*Spectroscopy of Porphyrins: Vibrational States*], Nauka i Tekhnika, Minsk, 1985, 416 pp. (in Russian).
8. L. J. Bellami, *The Infrared Spectra of Complex Molecules*, Chapman and Hall, London, 1975, 393 pp.
9. P. A. Stuzhin and O. G. Khelevina, *Coord. Chem. Rev.*, 1996, **147**, 41.
10. O. G. Khelevina, P. A. Stuzhin, I. S. Migalova, and O. V. Shukhto, *Zh. Obshch. Khim.*, 2001, **71**, 1738 [*Russ. J. Gen. Chem.*, 2001, **71** (Engl. Transl.)].
11. K. M. Kadish, B. Boisselier-Cocolios, P. Cocolios, and R. Guilard, *Inorg. Chem.*, 1985, **24**, 2139.
12. P. Cocolios, R. Guilard, D. Bayeul, and C. Lecomte, *Inorg. Chem.*, 1985, **24**, 2058.
13. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley and Sons, New York, 1978.
14. S. V. Zaitseva, S. A. Zdanovich, and T. A. Ageeva, *Molecules*, 2001, **5**, 1495.
15. J. C. Dobrowolski and M. H. Jamroz, *J. Mol. Struct.*, 1992, **275**, 211.
16. B. Aβmann, G. Ostendorp, and H. Homborg, *Z. Anorg. Allg. Chem.*, 1995, **621**, 1708.
17. K. Schweiger, A. Kienast, B. Latte, and H. Homborg, *Z. Anorg. Allg. Chem.*, 1997, **623**, 973.
18. B. Aβmann, A. Franken, and H. Homborg, *Z. Naturforsch.*, 1996, **51b**, 325.
19. H. Brand and J. Arnold, *Coord. Chem. Rev.*, 1995, **140**, 137.
20. R. D. Shannon and C. T. Prewitt, *Acta Crystallogr.*, 1969, **B25**, 925.

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