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Study of the Coordination Properties of Cobalt 5,15-Di(*ortho*-nitrophenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetrabutylporphyrinate in the Reaction with Nitrogen Organic Bases

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Abstract—The thermodynamics and kinetics of the formation of coordination compounds of cobalt(III) 5,15-di-(*ortho*-nitrophenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetrabutylporphyrinate with nitrogen organic bases in an inert solvent were studied. The type of the structure was determined, the stability and the degree of deformation of the molecular complex were estimated. The dependence of the coordination properties of the cobalt(III) 5,15-di(*ortho*-nitrophenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetrabutylporphyrinate on the electronic and conformational factors of the macrocycle was revealed. The geometry of the cobalt porphyrinate molecule and its molecular complexes was optimized by the PM3 method, the presence of steric strain in these molecules was found, and the binding energy of the metal atom to the N-base was calculated. A good agreement between the calculated and experimental data was demonstrated.

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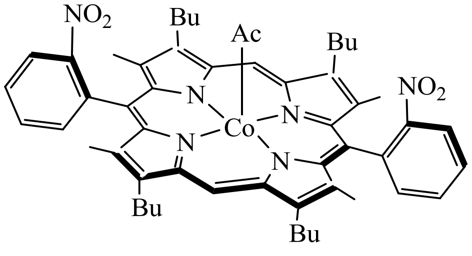
The interest in the highly charged metal porphyrinates is associated with the possibility of their use for obtaining new materials with desired properties for various catalytic, redox, and other processes [1–3]. The reactivity of the metal porphyrinates is largely associated with their coordination properties. Therefore, in order to develop the understanding of the effect of the structure and the degree of the coordination saturation of macrocyclic compounds on the stability of molecular complexes, we studied the process of axial binding of nitrogen organic bases by the cobalt(III) 5,15-di(*ortho*-nitrophenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetrabutylporphyrinate [(Ac)CoP] in benzene. As research methods we used spectrophotometric titration [4] and computer simulation [5–8].



(Ac)CoP

The process of coordination of N-bases by the cobalt di(*ortho*-nitrophenyl)octaalkyl-substituted porphyrinate [L = imidazole (Im), 2-methylimidazole (2-MeIm), pyridine (Py), and dimethylformamide (DMF)] proceeds according to equation (1) and is accompanied by a red shift of the main bands (B, Q1, Q2) in the electron absorption spectrum (EAS) of the metal porphyrinate (Fig. 1).

$$(Ac)CoP + L_n \underset{}{\overset{K_{eq}}{\rightleftarrows}} (Ac)Co(L)_nP. \qquad (1)$$

It is noteworthy that the molecular complex $(Ac)Co(L)_nP$ is formed relatively slowly, and this allowed us the determination of the rate of reaction (1). The effective rate constants of the formal first-order reaction found for the range of concentrations of Im, 2-MeIm, and Py are listed in Table 1. A linear dependence (2) of the effective rate constants on the concentration of an organic base (Fig. 2) is revealed, and the value of the true rate constant (Table 1) and the reaction order $m = 1$ with respect to the base ($m = 0.7$, 0.8, and 0.7 for imidazole, 2-methylimidazole, and pyridine, respectively) were determined.

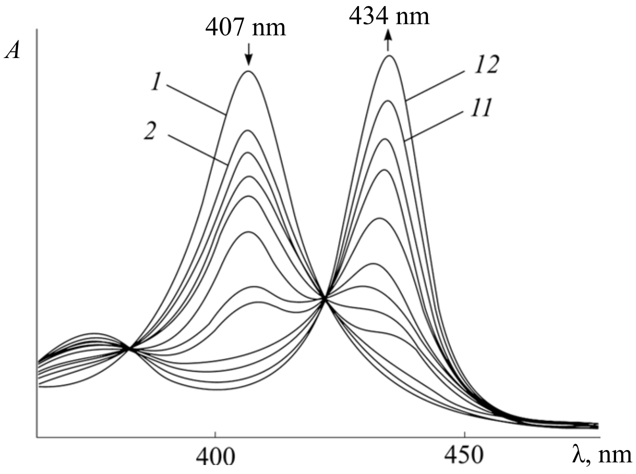


Fig. 1. Changes in the EAS of (Ac)CoP in the course of the reaction with 2-methylimidazole: (*1*) (Ac) CoP [$c_{(Ac)CoP} = 1.60\times10^{-6}$ M]; (*2–11*) (Ac)CoP with 2-methylimidazole in intermediate concentrations ($c_{2\text{-MeIm}} = 4.12\times10^{-5}$–$1.03\times10^{-3}$ M), (*12*) (Ac)CoP with excess imidazole ($c_{2\text{-MeIm}} = 4.03\times10^{-3}$ M) in benzene.

$$\log k_{ef} = \log k_1 + m\log [L]. \tag{2}$$

The rate equation has the form (3):

$$-dc_{(Ac)CoP}/dt = k_1[(Ac)CoP][L]. \tag{3}$$

It is shown that the rate of reaction (1) depends on the nature of the organic base. The highest rate is typical for the reactions involving imidazole (Table 1).

The change in the intensity and position of the main absorption bands in the EAS of cobalt porphyrinate in the course of the reaction (1) allows the use of spectrophotometric method for determining the equilibrium constant [Eq. (4), Table 2]. The composition of the final reaction product was determined by a limiting logarithmic method (Bent–French) [4] from the slope (tan α) of the linear dependence of $\log[(A_{eq}- A_0)/(A_\infty- A_{eq}]$ vs. $\log c_L$ (Fig. 3) and the change in the ^{1}H NMR spectrum. The value of n for all the bases is 0.9–1.1, which within the error equaes to one, that is, the ratio metal porphyrinate : N-base = 1:1.

$$K_{st} = \frac{(A_{eq}-A_0)/(A_\infty-A_0)}{(A_\infty-A_{eq})/(A_\infty-A_0)}\,\frac{1}{(c^0_L-c^0_{MP})[(A_{eq}-A_0)/(A_\infty-A_0)]}\,. \tag{4}$$

Comparing the data in Table 2 revealed the dependence of the stability of molecular complexes of cobalt porphyrinate on the donor–acceptor properties of small organic molecules. The values of K_{eq} increased in the series: (Ac)Co(DMF)P < (Ac)Co(Py)P < (Ac)Co(2-MeIm)P < (Ac)Co(Im)P.

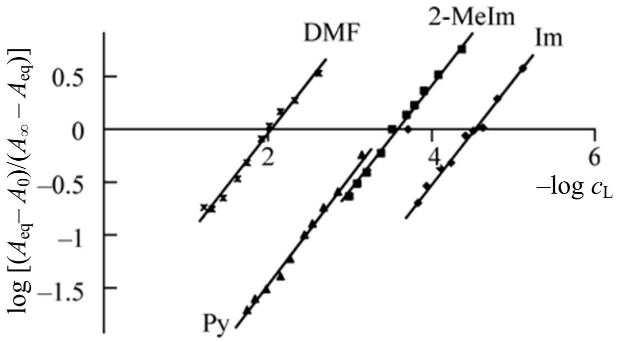


Fig. 2. Dependence of log $[(A_{eq}- A_0)/(A_\infty- A_{eq})]$ vs log c_L for the intermolecular interaction of (Ac)CoP with organic bases. A_0, A_{eq}, and A_∞ are optical densities of solutions at the working wavelength for the metalloporphyrin, the equilibrium mixture and the molecular complex, respectively.

As an index of basically we take the values of pK_a [9] and proton affinity (E_{prot}) of the N-bases molecules in the gas phase [10] calculated by the quantum-chemical method AM1 [8] (Table 2). It is noticeable that for 2-methylimidazole the change in the donor–acceptor properties in going from the aqueous phase to organic media is typical, since the value of E_{prot} is not consistent with the pK_a [9]. The proton affinity

Table 1. Kinetic parameters of reaction (1) with the N-bases imidazole, 2-methylimidazole, and pyridine

$c_{(Ac)CoP}$ 2.40×10^{-6}, M	
$c_{Im}\times10^5$, M	k_{ef}, 10^6, s^{-1}
2.38	7.0
3.81	8.9
5.94	13.0
7.92	15.8
k_1 1.1×10^{-2}, s^{-1} mol^{-1} l	
$c_{(Ac)CoP}$ 1.60×10^{-6}, M	
$c_{2\text{-MeIm}}\times10^4$, M	k_{ef}, 10^6, s^{-1}
1.24	2.20
4.12	7.20
8.24	9.80
k_1 3.38×10^{-3}, s^{-1} mol^{-1} l	
$c_{(Ac)CoP}$ 1.87×10^{-6}, M	
$c_{Py}\times10^3$, M	k_{ef}, 10^5, s^{-1}
0.71	0.31
2.84	1.12
5.33	1.71
10.70	2.16
14.20	2.76
k_1 6.13×10^{-4}, s^{-1} mol^{-1} l	

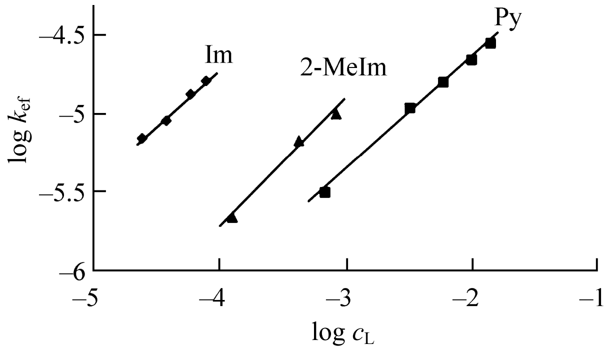


Fig. 3. Dependence of the effective rate constant for reaction (1) on the concentration of organic base.

increases in the series of the bases: DMF < Py < Im < 2-MeIm (Table 2). Thus, an increase should be expected in the stability of the complex (Ac)Co(2-MeIm)P compared with (Ac)Co(Im)P. However, at the coordination of the 2-MeIm molecule by the cobalt porphyrinate a steric interference arises caused by the presence of a methyl group and its orientation near the active site of the N-base. Therefore, the stability of (Ac)Co(2-MeIm)P is much lower (Table 2). Linear dependences of K_{eq} vs pK_a and E_{prot} (Fig. 4) are revealed, which are described by the correlation: log K_{eq} = 0.56 pK_a + 0.56 (r = 0.99) and log K_{eq} = –0.12, E_{prot} –16.87 (r = 0.99), respectively.

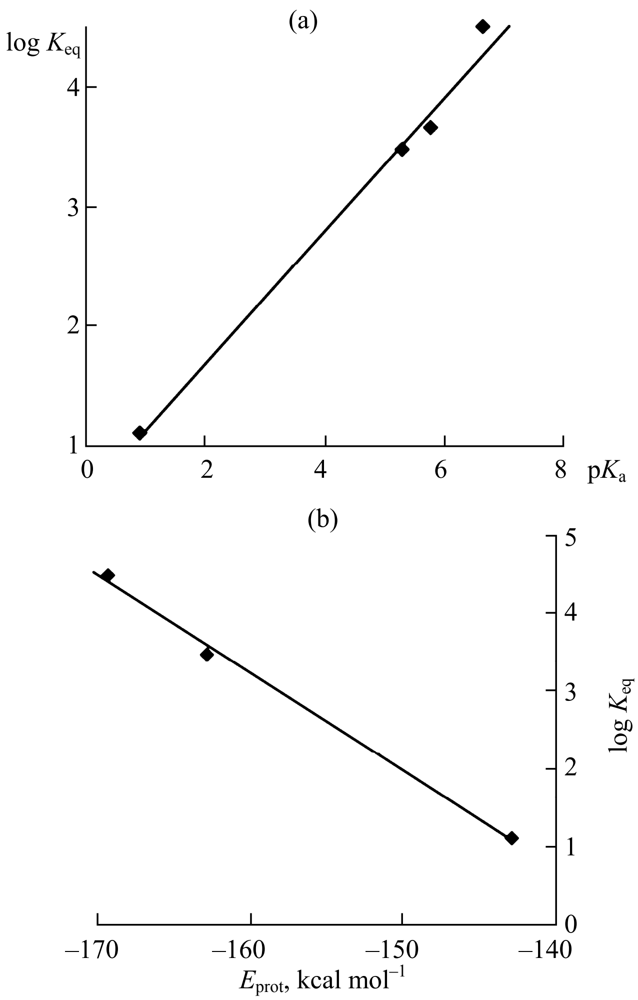


Fig. 4. The dependence of the stability of the complexes (Ac)Co(L)P on the (a) pK_a and the calculated protonation energy of the organic bases (b).

Comparing the values of K_{eq} for the investigated cobalt porphyrinate (Table 2) and its zinc analog [11], we found that the stability of molecular complexes (Ac)CoP is lower than that of zinc complexes. This is due to the nature of the metal atom and the presence of acetate ion in the coordination site of the cobalt porphyrinate, which contributes to the *cis*- and *trans*-effects of ligands in the macrocyclic compound. A significant impact on the stability renders also the conformation of the macrocycle. The steric strain of (Ac)CoP is higher than that in the zinc analog (Fig. 5). The greater is the degree of deformation of the macrocycle, the lower its aromaticity and, accordingly, the higher its basicity.

The deformation distortions of the macrocycle of cobalt porphyrinate and its molecular complexes were assessed by the analysis of the data calculated by the quantum-chemical method RM3 [5–8]. The calculations imply that the (Ac)CoP molecule is nonplanar, the predominant deformation is of the saddle-shaped type (Figs. 5, 6). The coordination unit of (Ac)CoP has C_{4v} symmetry and is arranged as a tetragonal pyramid with a rhombus in the basis. The average value of the deviation of the macrocycle skeletal atoms from its mid-plane (XY) along the Z-axis is 0.41 Å.

Considering the calculated characteristics of the optimized molecules of the compounds under the study (Table 3, Fig. 6) we found that the existence of the cobalt porphyrinate molecular complex of the composition (Ac)Co(L)P is energetically favorable. The

Table 2. Stability constants of molecular complexes (Ac)Co(L)P, and basicity indices of the extra ligand

Complex	K_{eq}^{298}×10^{-3}, mol^{-1} l	pK_a	–E_{prot}, kcal mol^{-1}
(Ac)Co(Im)P	31.0±3.25	6.65	169.36
(Ac)Co(2-MeIm)P	4.95±0.42	5.89	173.06
(Ac)Co(Py)P	2.95±0.23	5.29	162.79
(Ac)Co(DMF)P	0.013±0.001	0.92	142.92

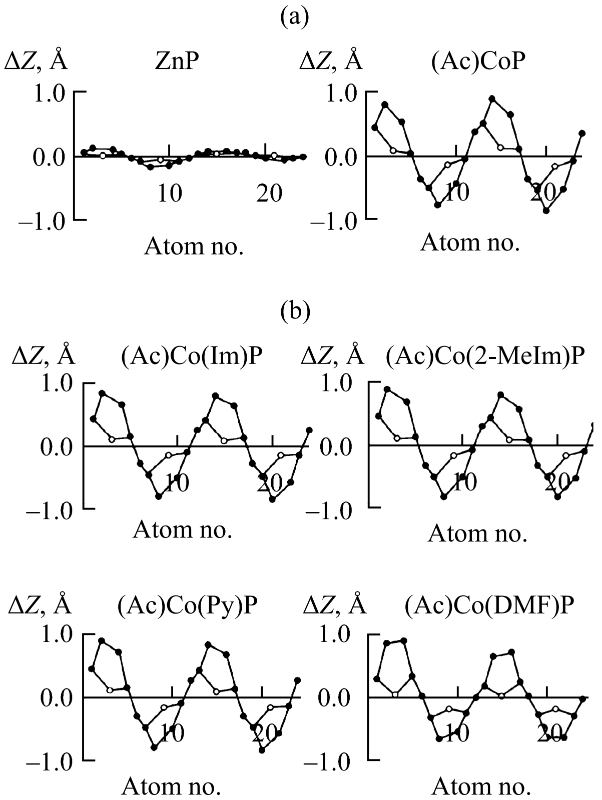


Fig. 5. Deviation of the skeletal atoms of the porphyrin macrocycle along the Z axis from its mean plane for the compounds: (a) zinc 5,15-di(*ortho*-nitrophenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetrabutylporphyrinate and cobalt(III) 5,15-di(*ortho*-nitrophenyl)octaalkyl-substituted porphyrinate, (b) molecular complexes (Ac)Co(L)P, according to quantum-chemical calculation by PM3; (open circles): the nitrogen atoms, (filled circles): the carbon atoms.

base is coordinated at the side opposite to the acido ligand, therewith occurs a change in the degree of deformation of the macrocycle, but its type and symmetry remain the same (Fig. 6).

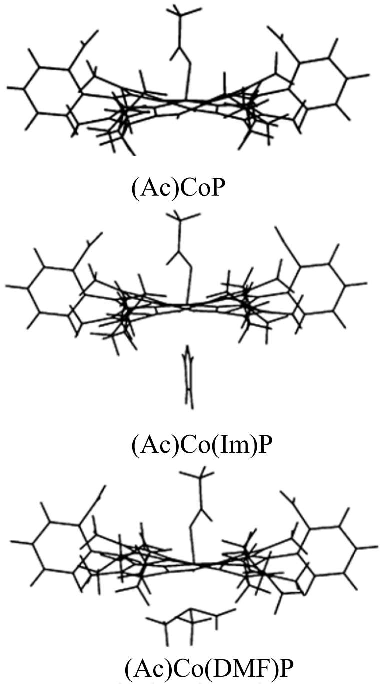


Fig. 6. The structure of (Ac)CoP and its molecular complexes with imidazole and DMF calculated by the quantum-chemical method PM3.

Analysis of the data in Tables 2 and 3 revealed a correlation between the energy of the Co–L bond (E_b) and the complex stability. The dependence is linear and is described by the equation: $\log K_{eq} = –0.14$, E_b –4.44 ($r = 0.99$) (Fig. 7).

The results of the study of the intermolecular interactions of cobalt porphyrinate with N-bases show that the stability of the complexes depends on the electronic and geometric structure of both the porphyrin ligand and the small organic molecule. The cobalt porphyrinate possesses sufficient selectivity to

Table 3. Selected geometric and energy characteristics of (Ac)CoP and its molecular complexes

Complex	$-E_{b\,Co–L}$, kcal mol^{-1}	Bond length, Å					
		Co–N^1 Co–N^3	Co–N^2 Co–N^4	N^1–N^3 N^2–N^4	Co–L	Co–Ct	P^a
(Ac)CoP		1.921	1.923	3.858		0.285	10.881
		1.926	1.922	3.802			
(Ac)Co(Im)P	65.04	1.947	1.947	3.887	1.929	0.099	11.021
		1.944	1.951	3.894			
(Ac)Co(2-MeIm)P	61.25	1.945	1.951	3.892	1.933	0.134	11.030
		1.955	1.944	3.895			
(Ac)Co(Py)P	58.20	1.953	1.951	3.894	1.940	0.136	11.057
		1.950	1.954	3.902			
(Ac)Co(DMF)P	40.80	1.940	1.960	3.895	2.136	0.140	11.120
		1.960	1.940	3.885			

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

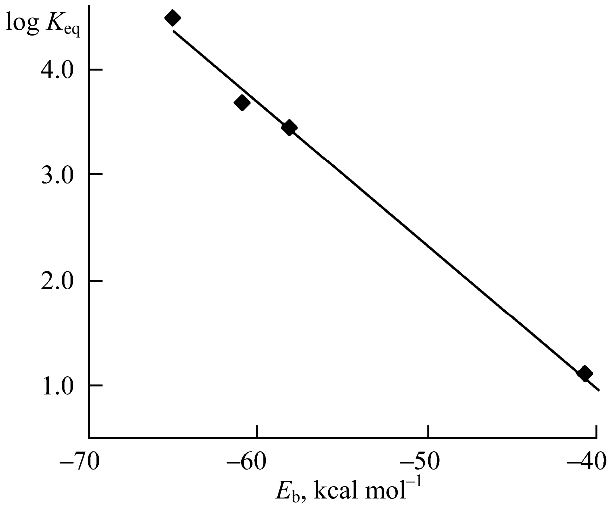


Fig. 7. The dependence of the stability of complexes (Ac)Co(L)P on the value of E_b.

the donor–acceptor interaction, which allows using it for the creation of self-organizing systems with desired properties.

EXPERIMENTAL

The equilibrium (stability) constant K_{eq} of the studied reaction was determined by the method of [12] at 298 K, solvent benzene.

The electron absorption spectra (EAS) were recorded on a Cary-50 spectrophotometer in the range from 380 to 700 nm. The optical density of a series of solutions at a constant concentration of cobalt(III) porphyrinate and various concentrations of organic base was recorded at the operating wavelengths 407–434 nm from a cell 1 cm thick. The accuracy of the temperature control was within 1K. The calculation of K_{eq} and the calculation of the mean-square deviations was carried out by the method of least-squares using the Microsoft Excel program. The relative error in determining the required quantities was 5–12%.

Quantum-chemical calculations were performed by PM3 method [5–8] using the PC-version [13] of the Gamess software package [14]. The condition of the termination of the calculation was the pre-defined gradient value 0.0004 kJ mol^{-1} Å^{-1}. The preparation of input data and processing calculation results was performed using the program ChemCraft version 1.3 [15]. For the initial approximation the averaged data on the structure of metals porphyrinates were taken [16]. Bond lengths and bond angles for the alkyl substituents and organic bases correspond to the published data [17]. The orientation of aromatic bases was set so that the nitrogen atom with its unshared electron pair was directed toward the cobalt atom.

5,15-Di(*ortho*-nitrophenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetrabutylporphyrin was synthesized according to [18].

The cobalt complex of 5,15-di(*ortho*-nitrophenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetrabutylporphyrin (Ac)CoP was synthesized by the reaction of the porphyrin ligand with a tenfold excess of cobalt acetate in boiling acetonitrile over 2 to 2.5 h. The reaction monitoring was carried out by observing the changes in the electron absorption spectrum of the mixture. About the reaction completeness we judged by the disappearance of the absorption bands of porphyrin and the increase in the absorption bands of its cobalt complex. After the reaction completion acetonitrile was distilled off and the dry residue was dissolved in benzene. The benzene solution was washed with water and evaporated. The complex was purified by chromatography on silica gel (eluent benzene) followed by recrystallization from chloroform. R_f (Silufol): 0.80 (benzene). EAS, λ_{max}, nm (log ε): 565 (4.24), 535 (4.02) 407 (5.09) (benzene). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 9.90 s (2H, *meso*-H), 8.53 d (2H, *ortho*-H, phenyl), 7.99 m (6H, *para,meta*-H, phenyl), 3.84 t (8H, CH_2, butyl group), 2.12m (8H, CH_2, butyl group), 1.77m (8H, CH_2, butyl group), 1.10 t (12H, CH_3, butyl group), 2.40s (12H, CH_3, methyl group), 2.36 s (3H, CH_3CO_2). Found, %: C 68.40, H 6.50, N 8.83. $C_{54}H_{61}CoN_6O_6$. Calculated, %: C 68.34, H 6.48, N 8.86.

Complex (Ac)Co(2-MeIm)P. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 9.64s (2H, *meso*-H), 8.38d (2H, *ortho*-H, phenyl), 7.90 m (6H, *para,meta*-H, phenyl), 3.80 t (8H, CH_2, butyl group), 2.08 m (8H, CH_2, butyl group), 1.68 m (8H, CH_2, butyl group), 1.08 t (12H, CH_2, butyl group), 2.36 s (12H, CH_3, methyl group), 2.30 s (3H, CH_3CO_2), 2-MeIm: 6.93s (2H in 4,5 positions), 2.41 s (3H, CH_3, methyl group).

Complex (Ac)Co(Py)P. ^{1}H NMR spectrum ($CDCl_3$) δ, ppm: 9.83 s (2H, *meso*-H), 8.04 d (2H, *ortho*-H, phenyl), 7.88 d (2H, *para*-H, phenyl), 7.82 t (4H, *meta*-H, phenyl), 3.85 t (8H, CH_2, butyl group), 2.07 m (8H, CH_2, butyl group), 1.57 m (8H, CH_2, butyl group), 1.03 t (12H, CH_2, butyl group), 2.34 s (12H, CH_3 methyl group), 2.27 t (3H, CH_3CO_2), Py: 8.51 s (2H, *ortho*-H), 7.64 s (3H, *para,meta*-H).

Complex (Ac)Co(DMF)P. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 9.99 s (2H, *meso*-H), 9.17d (2H, *ortho*-H, phenyl), 9.11d (2H, *para*-H, phenyl), 8.96 t (4H, meta-H, phenyl), 4.52 t (8H, CH_2, butyl group), 2.32 m (8H, CH_2, butyl group), 1.76 m (8H, CH_2, butyl group), 1.58 t (12H, CH_3, butyl group), 2.74 s (12H, CH_3, methyl group), 2.18 s (3H, CH_3CO_2), DMF: 7.50 s (H, COH), 2.85 s (3H, CH_3), 2.76s (3H, CH_3).

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