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Effect of Ligands on the Formation Equilibrium of the Dioxygen Carrier in the Co(II)–Bidentate Schiff Base–Amine System

B. JEZOWSKA-TRZEBIATOWSKA, P. CHMIELEWSKI* and A. VOGT

Institute of Chemistry, University of Wrocław, Wrocław, Poland

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Abstract

The effect of ligands on the formation equilibrium of a pentacoordinated, high-spin $Co(BSB)_2B$ complex (BSB = bidentate Schiff base, B = amine) in organic solvent (toluene, DMF) was investigated. The equilibrium constant K_B was found to depend on the magnitude of the steric hindrance occurring in both the axial and equatorial ligand. For axial ligands of a similar structure the equilibrium constant was found to roughly depend on their basicities. For a row of equatorial ligands a negative correlation between the electron density on the cobalt ion and the formation equilibrium constant of a pentacoordinated complex was shown. Hammett relationships between log K_B values and σ constants were observed for the substituents X and Y on the phenyl rings of Co(sal-Y-anil)$_2$ and Co(X-salbut)$_2$ with the reaction constants $\rho_1 = 1.50$ and $\rho_2 = 0.93$, respectively.

Our conclusions may shed some light on the question of the electron state of a complex capable of binding oxygen, and on a more general problem of equilibria for high-spin tetrahedral complexes in solution.

Introduction

The cobalt(II) complexes with bidentate Schiff bases are high-spin compounds of a distorted tetrahedral structure, both in solid state and dissolved in non-coordinating solvents [1–3]. In coordinating solvents, such as pyridine, they are octahedral unless there is a significant steric hindrance in the chelating ligand.

As was reported earlier [4] these complexes are capable of reversible binding of oxygen in solution in the presence of a slight excess of amine. Here we discuss the effect of ligands on the formation of a complex capable of binding dioxygen formed in the $Co(BSB)_2$–B–organic solvent system (BSB = bidentate Schiff base, B = amine). The purpose of our present studies was to determine the effect of donor–acceptor and steric factors occurring in ligands on the equilibrium constant (1) which, as was shown, takes place in the system under investigation [4]:

$$\mathrm{Co(BSB)_2 + B \overset{K_B}{\rightleftharpoons} Co(BSB)_2B} \qquad (1)$$

Experimental

Abbreviations for the ligands used in this paper are as follows (structure of the ligands and numbering of the carbon atoms is shown in Fig. 1): salprop-R = n-C_3H_7, salbut-R = n-C_4H_9, sal i-but-R = i-C_4H_9, sal s-but-R = s-C_4H_9, sal t-but-R = t-C_4H_9, salpen-R = n-C_5H_{11}, salnon-R = n-C_9H_{19}, salcet-R = n-$C_{16}H_{33}$, salchx-R = c-C_6H_{11}, salall-R = C_3H_5, salben-R = $CH_2C_6H_5$, sal M-prop-R = 3-(1-morpholylo)-C_3H_6, salanil-Ar = C_6H_5, sal 2'-Meanil-Ar = 2'-$CH_3C_6H_4$, sal 3'-Meanil-Ar = 3'-$CH_3C_6H_4$, sal 4'-Meanil-Ar = 4'-$CH_3C_6H_4$, sal 4'-MeOanil-Ar = 4'-$CH_3OC_6H_4$, sal 4'Clanil-Ar = 4'-ClC_6H_4, sal 4'-N(Me)$_2$anil-Ar = 4'-$N(CH_3)_2C_6H_4$ (for all these ligands X = H); 3-Mesalbut-X = 3-CH_3, 4-Mesalbut-X = 4-CH_3, 5-Mesalbut-X = 5-CH_3, 3-MeOsalbut-X = 3-OCH_3, bensalbut-X = 5,6-benzo, 5-Clsalbut-X = 5-Cl, 5-NO_2-salbut-X = 5-NO_2 (for all these ligands R = n-C_4H_9).

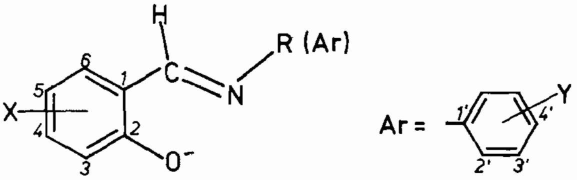

Fig. 1. Structure of the BSB ligands.

The Co(salanil)$_2$, Co(sal2'-Meanil)$_2$, Co(sal3'-Meanil)$_2$, Co(sal4'-Meanil)$_2$, Co(sal4'-MeOanil)$_2$, Co-[sal4'-N(Me)$_2$anil]$_2$, Co(sal4'-Clanil)$_2$, Co(sal s-but)$_2$, Co(sal t-but)$_2$, Co(salchx)$_2$ complexes were synthesized by mixing equimolar amounts of salicylaldehyde and the appropriate amine in methanol solution. The ligand solution formed was alkalized with a stoichiometric quantity of sodium methylate and

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*Author to whom correspondence should be addressed.

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then cobalt acetate solution in methanol was added dropwise in a stoichiometric ratio of 1:2. The precipitated complex was filtered off, washed with methanol, dried and recrystallized from toluene. Other complexes were synthesized in a similar way but under inert gas because of their sensitivity to oxygen. All complexes showed satisfactory agreement of their elemental analyses with the theoretical content of particular elements.

Salicylaldehyde, 3-methoxysalicylaldehyde, naphthylsalicylaldehyde and 5-nitrosalicylaldehyde (Merck) were used without purification. 3-, 4-, 5-methylsalicylaldehyde and 5-chlorosalicylaldehyde were obtained by the Duff reaction [5]. The amines employed for syntheses were used without purification. Liquid amines used for measurements were distilled prior to use; solid amines were recrystallized from toluene.

Toluene was purified by standard methods and was distilled over sodium prior to use. Dimethylformamide was purified by distilling the heteroazeotrope DMF–benzene–water and distilled over CaH_2 under reduced pressure and stored over molecular sieves.

Spectrophotometric measurements were carried out on a Cary 14 spectrophotometer provided with a thermostatted attachment. The temperature measuring error was 0.5 °C. Complex samples were weighed in a cell closed with a silicone rubber stopper. After removing air from the cell some deoxygenated solvent was injected in to it. The cell filled in this way was reweighed for accurate determination of the amount of solvent. Amines (or their solutions) were added by means of microsyringe (Hamilton). The amount of amine added was also corrected by weight.

Results and Discussion

The electronic spectra of all studied complexes are in the near IR region. They show the presence of two absorption bands (the components of $^4T_2(F) \rightarrow {}^4T_1$-(F) transition in the idealized tetrahedral symmetry [3, 6]), at 1300 and 975 nm in toluene and 1250 and 900 nm in DMF solutions. Molar extinction coefficients ϵ for the main maximum ~1300 nm are as follows: 48 for $Co(salben)_2$, 50 for $Co(salall)_2$ and 67, 72, 82 for $Co(salchx)_2$, $Co(sal\ s\text{-}but)_2$, $Co(sal\ t\text{-}but)_2$ respectively. For the other complexes ϵ is equal to 55 ± 3. The value of ϵ does not depend on solvent, with the exception of $Co(5\text{-}NO_2salbut)_2$ (*vide infra*).

The similarity of electronic spectra of all studied complexes indicates their similar structure regardless of the substituents. Results of the earlier studies on some of these complexes [2, 3] revealed that they are high-spin and have the tetragonally distorted tetrahedral structure.

In order to investigate the equilibria existing in the $Co(BSB)_2$–B–solvent system, changes in the electronic spectra of complexes over the 500–2000 nm region were used (Fig. 2). On increasing the amine concentration one can observe a decrease in absorbance of the bands at about 1300 and 900 nm, characteristic of the tetrahedral $Co(BSB)_2$ complexes. The amine concentration was varied from about 0.3:1 to 20:1 with respect of the starting complex. The spectra show isosbestic points, thus proving the existence of two absorbing species in equilibrium. The amine concentration range over which this state is maintained depends on the type of complex, amine and solvent. Any further increase in amine concentration results in the formation of a new, much weaker (about tenfold) band at about 1000 nm (Fig. 2), characteristic of the hexacoordinated high-spin $Co(BSB)_2(B)_2$ complexes [2, 3]. The isosbestic point ceases to exist, and hence at least three complexes are in equilibrium. Thus, at higher amine concentrations apart from equilibrium (1) consecutive equilibrium (2) also occurs in the system under investigation.

$$Co(BSB)_2B + B \overset{K_{2B}}{\rightleftharpoons} Co(BSB)_2(B)_2 \qquad (2)$$

The absorbance of the main band (*ca.* 1300 nm) was assumed to be a measure of the tetrahedral complex concentration. For the amine concentration range where only two complexes occur the law of mass action for equilibrium (1) assumes the following form:

$$\frac{A_0 - A}{A} = K_B[B] \qquad (3)$$

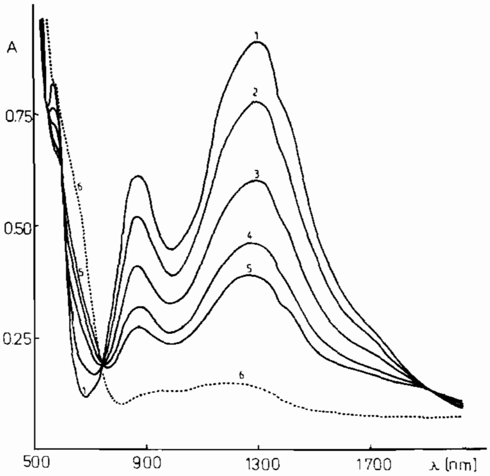

Fig. 2. Electronic spectra of the $Co(5\text{-}Mesalbut)_2$–1-MeIm system in toluene at various amine concentration c_B: 1) 0.0; 2) 9.38 × 10^{-3} M; 3) 0.02608 M; 4) 0.04840 M; 5) 0.06499 M; 6) 0.2682 M; c_0 = 0.01535 M, T = 25 °C.

where A = absorbance at the maximum for a solution of given amine concentration [B]

A_0 = absorbance of solution for [B] = 0.

Equilibrium amine concentration [B] may be determined as follows:

$$[B] = c_B - [Co(BSB)_2B] = c_B - \frac{A_0 - A}{\epsilon l}$$

where c_B = total concentration of the amine added
ϵ = molar extinction coefficient
l = length of optical path in cm.

On plotting the relationship $(A_0 - A)/A$ *versus* [B] a straight line is obtained in the above mentioned amine concentration range. Its slope is equal to K_B. Typical experimental plots are presented in Fig. 3.

With regard to low value of K_B we decided to use eqn. (3) instead of the relation $\log[(A_0 - A)/A]$ *vs.* log [B] usually used for K_B determination. The eqn. (3) gives K_B values as the slope of the straight line, while in log–log relation the log K_B is the intercept of line with slope equal to 1. The value of intercept is very sensitive on a random scatter of data points because the points for small $(A_0 - A)/A$ and [B] value (estimated with the largest error) have the greatest weight in the least square method for the log–log relation.

The rectilinearity of the plots presented in Fig. 3. is not the only proof that a complex of coordination number 5 occurs in the system under investigation. We have not observed a spectrum characteristic of the high-spin pentacoordinated complexes [7, 8]. There is, however, an indirect confirmation for the formation of such a complex in the studied system. The $Co(salben)_2(MeIm)_2$ complex precipitated from toluene solution at a 3-fold excess of amine with respect to the initial compound interacts with oxygen neither in solids nor in solution. The initial tetrahedral complex $Co(salben)_2$ undergoes only slow irreversible oxidation in solution. On the other hand, at slight excess of amine (about 1:1.3) oxygen is found to be reversibly bound. The above summary of experimental facts shows that the oxygen-binding system may be only a complex of coordination number 5.

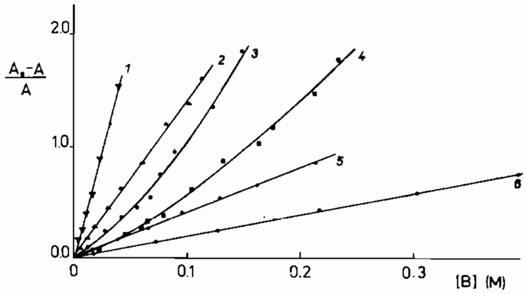

Fig. 3. Plots of $(A_0 - A)/A$ *vs.* [B] for the $Co(salbut)_2$–B–toluene system at 25 °C; B = 1) 1-MeIm; 2) pyrr; 3) $4\text{-}CH_3py$; 4) py; 5) pip; 6) morph.

Over the amine concentration range in which three complexes occur one can assume:

$$\frac{A_0 - A}{A} = K_B[B] + K_BK_{2B}[B]^2 \qquad (4)$$

In this case the equilibrium amine concentration should be calculated by means of an iterative procedure. Equation (4) may of course only be applied if the absorbance of the hexacoordinated complex is negligible. For the systems investigated by us this equation was applicable only in the case of weakly coordinating axial ligands (pyridine and 4-picoline) for which the equilibrium of three complexes occurs over the entire amine concentration range under investigation (6×10^{-3}–0.2 M by concentration of starting complex c_0 = 0.01 M). The dependence of $(A_0 - A)/A$ *vs.* [B] is in this case a second degree curve (Fig. 3).

The K_B constants determined by the least squares method are presented in Tables I–IV.

Table I contains the values of K_B constants for various axial ligands in comparison with the pK_a values of protonated amines. Over the entire group of axial ligands under investigation there is no correlation between basicity and ability for coordination. This results from differences in the structure of ligands, particularly from different steric hindrances. The effect of the steric factor is visible in the n-

TABLE I. Equilibrium Constants for the Binding of the Axial Ligands to $Co(salbut)_2$ Complex.

B[a]	$K_B[M^{-1}]$		pK_a[b]
	Toluene, 25 °C	DMF, 2 °C	
$n\text{-}BuNH_2$	6.0 ± 0.3	3.84 ± 0.03	10.64
$s\text{-}BuNH_2$	2.11 ± 0.01	1.16 ± 0.02	10.56
$t\text{-}BuNH_2$	1.06 ± 0.02	0.25 ± 0.02	10.68
pip	3.99 ± 0.06	1.34 ± 0.04	11.12
morph	1.90 ± 0.02	0.65 ± 0.03	8.49
pyrr	15.3 ± 0.2	4.42 ± 0.09	11.30
1-MeIm	34.2 ± 1.0	9.18 ± 0.11	7.06
4-CNpy	3.40 ± 0.08		1.86[c]
py	3.81 ± 0.05	0.71 ± 0.02	5.25
$4\text{-}CH_3py$	8.01 ± 0.16	0.86 ± 0.05	6.03
$4\text{-}NH_2py$	82 ± 20[d]	13.43 ± 0.15	9.11

[a] $n\text{-}BuNH_2$ = n-butylamine; $s\text{-}BuNH_2$ = sec-butylamine; $t\text{-}BuNH_2$ = tert-butylamine; pip = piperidine; morph = morpholine; pyrr = pyrrolidine; 1-MeIm = 1-methylimidazole; 4-CNpy = 4-cyanopyridine; py = pyridine; $4\text{-}CH_3py$ = 4-picoline; $4\text{-}NH_2py$ = 4-aminopyridine. [b] Data from ref. [10], unless otherwise noted. [c] K. Schofield, 'Hetero-Aromatic Nitrogen Compounds', Plenum Press, New York, p. 146, 1967. [d] The great estimating error is due to low solubility of $4\text{-}NH_2py$ in toluene.

TABLE II. Equilibrium Constants for the Binding of 1-Methylimidazole to Co(BSB)$_2$ Complexes with Aliphatic Substituents.

Complex	K_B [M^{-1}]	
	Toluene, 25 °C	DMF, 2 °C
Co(salprop)$_2$	42.3 ± 1.6	9.5 ± 0.1
Co(salbut)$_2$ [a]	34.2 ± 1.0	9.2 ± 0.1
Co(sal i-but)$_2$	57.5 ± 3.1	10.4 ± 0.2
Co(sal s-but)$_2$	0.38 ± 0.02	0.12 ± 0.02
Co(sal t-but)$_2$	0.16 ± 0.03	<0.1
Co(salchx)$_2$	0.24 ± 0.01	0.12 ± 0.02
Co(salpen)$_2$	28.9 ± 0.5	7.2 ± 0.2
Co(salnon)$_2$	45.2 ± 1.2	
Co(salcet)$_2$	33.4 ± 0.8	
Co(sal M-prop)$_2$	49.9 ± 0.5	
Co(salall)$_2$	92.8 ± 5.0	22.3 ± 0.5
Co(salben)$_2$	96.4 ± 2.6	29.9 ± 0.8

[a] Data from Table I.

TABLE III. Equilibrium Constants for the Binding of 1-Methylimidazole to the Co(sal Y-anil)$_2$-type Complexes.

Y	K_B [M^{-1}]	
	Toluene, 25 °C	DMF, 2 °C
4'-N(CH$_3$)$_2$	2.35 ± 0.02	1.15 ± 0.05
4'-CH$_3$	8.3 ± 0.3	8.0 ± 0.1
4'-OCH$_3$	9.37 ± 0.3	8.55 ± 0.07
3'-CH$_3$	15.8 ± 0.3	8.6 ± 0.2
H	17.0 ± 0.3	19.2 ± 0.3
2'-CH$_3$	24.5 ± 0.5	8.9 ± 0.1
4'-Cl [a]	117 ± 20	81 ± 15

[a] The great estimating error is due to low solubility of Co(sal 4'-Clanil)$_2$ in both solvents.

TABLE IV. Equilibrium Constants for the Binding of 1-Methylimidazole to the Co(X-salbut)$_2$-type Complexes.

X	K_B [M^{-1}] Toluene, 25 °C
5-CH$_3$	23.4 ± 0.7
4-CH$_3$	24.9 ± 0.3
3-CH$_3$	27.8 ± 0.3
H [a]	34.2 ± 1.0
5,6-benzo	48.7 ± 1.4
3-OCH$_3$	94.7 ± 3.0
5-Cl	111.7 ± 2.3
5-NO$_2$	1140 ± 70

[a] Data from Table I.

BuNH$_2$–s-BuNH$_2$–t-BuNH$_2$ series (abbreviations are explained under Table I), in which the value of K_B decreases with the increasing steric hindrance at comparable basicity. However, the effect of donor properties may be observed on comparing the ligands of similar structures, *e.g.* morpholine, piperidine or 4-CN-pyridine; pyridine, 4-picoline, 4-NH$_2$-pyridine where an increase in basicity is accompanied by an increase in K_B.

The effect of an equatorial ligand on the stability constant of a pentacoordinated complex was investigated for 1-methylimidazole as an axial ligand (Tables II–IV).

For the complexes containing ligands of large steric hindrances in the form of substituents on the α-carbon of the chain attached to the azomethine group [Co(sal s-but)$_2$, Co(sal t-but)$_2$, Co(salchx)$_2$] the K_B constants are extremely low (Table II). The steric effect is related only to the adjacent surroundings of the azomethine group since neither the substituents on further carbons nor the chain length have any systematic effect on the value of K_B.

For the complexes in which no significant steric hindrance occurs there is a relationship between the donor properties of the chelating ligands and the value of K_B. This is particularly evident in toluene solutions. For the complexes with aliphatic substituents [Co(salben)$_2$, Co(salall)$_2$, Co(sal i-but)$_2$, Co(salprop)$_2$, Co(salbut)$_2$, Co(salpen)$_2$] the value of pK_a of the initial amine [9, 10] condensed in a Schiff base was taken as a measure of the donor properties of the nitrogen fragment in the ligand. There is a fairly strong negative correlation between the values of pK_a and log K_B (Fig. 4).

For the complexes of aromatic substituents on azomethine group (Table III) the Hammett equation is satisfied (Fig. 5). The reaction constant $\rho_1 = 1.50 \pm 0.07$ for toluene solutions at 25 °C was established using least squares method to the eqn. 5 which is corrected for the presence of two substituents Y on the ligands [11]. The σ^0 substituent constants were taken for the best fit [12].

$$\log K_B{}^Y = \log K_B{}^H + 2\rho_1\sigma_Y \tag{5}$$

The Hammett relationship is also observed for complexes of the Co(X-salbut)$_2$ type (Table IV), if substituents on the salicylate fragment of the ligand are in *para* and *meta* positions with respect to the

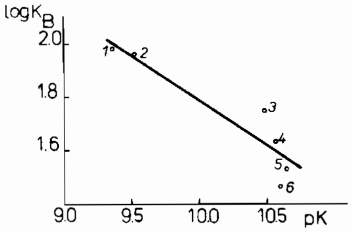

Fig. 4. Correlation of log K_B (toluene, 25 °C) with pK_a of the parent amine of the Schiff base. B = 1-MeIm, BSB = 1) salben; 2) salall; 3) sal i-but; 4) salprop; 5) salbut; 6) salpen. Correlation coefficient $r = -0.922$, t = 4.76.

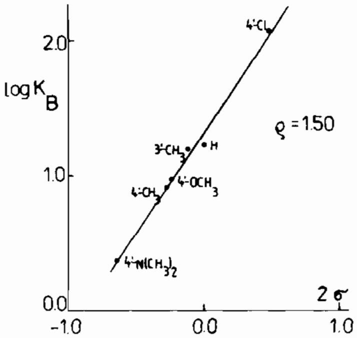

Fig. 5. Plot of log K_B *vs.* 2σ for the addition of 1-MeIm to Co(sal Y-anil)$_2$ (toluene, 25 °C).

phenolic oxygen atom *i.e.* 4, 5, 6 positions (Fig. 6). Reaction constant ρ_2 = 0.93 ± 0.02 was established by the same method as the ρ_1 value.

The fact that ρ_1 and ρ_2 are positive shows that the electron density decrease on cobalt ion favours the coordination of an axial ligand, making the complex a stronger Lewis acid.

The effect of solvent on the K_B constant is markedly significant. In a polar solvent, DMF, coordination of the fifth position is difficult owing to complex solvation, as reported earlier [4]. DMF is not capable of coordination with the cobalt ion apart from the Co(5-NO$_2$salbut)$_2$ complex whose electronic spectrum in DMF differs markedly from that in toluene and is characteristic of a hexacoordinated complex. Also the PMR spectrum of that complex in DMF-d$_7$ differs from that in CDCl$_3$, whereas for other complexes the spectra in both solvents are similar [13]. The diffuse reflectance spectrum of Co(5-NO$_2$-salbut)$_2$ shows that also in the solid the cobalt ion occurs in a hexacoordinated environment, since it is identical with the diffuse reflectance spectrum of Co(salben)$_2$(MeIm)$_2$ prepared by us, and with the spectrum of dipyridine adducts prepared earlier by other authors [1, 14]. This may result from coordination of the nitro groups in the crystal lattice of the complex.

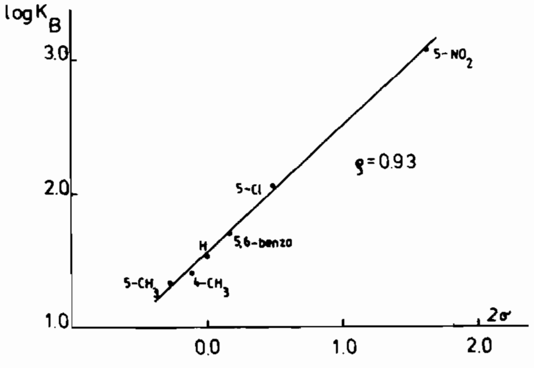

Fig. 6. Plot of log K_B *vs.* 2σ for the addition of 1-MeIm to Co(X-salbut)$_2$ (toluene, 25 °C).

Conclusions

The results obtained indicate that the stability constant of a pentacoordinated complex (K_B) depends on the steric hindrance of the axial and equatorial ligand and on their donor–acceptor properties. The nature of the steric hindrance disturbs the existing tendencies and, therefore, when discussing the effect of ligands one should have in view that the ligand compared would have a similar structural nature at least close to that of donor atoms.

The effect of the axial ligand on the stability of pentacoordinated complex was systematically investigated by Walker [15] for low-spin Co(II) complexes with *p*-methoxy-*meso*-tetraphenylporphyrin. The conclusions drawn from these studies on the correlation of the K_B values and basicity of the axial ligand and on the effect of its steric hindrance are similar to our, rather qualitative observations.

The formation in the case of weakly coordinated ligands of low basicity (py, 4-Mepy), of six-coordinated complexes Co(BSB)$_2$(B)$_2$, already at small (about 2-fold) excess in relation to the starting complex, could be interpreted as being an influence of the π-acceptor properties of these ligands. Empty pπ orbitals of pyridine nitrogen are able to overlap with filled dπ (d$_{xz}$, d$_{yz}$) metal orbitals, causing the reduction of the repulsive interaction between sixth ligand and metal through the decreasing of electron density on the cobalt ion. Thus, the d$_{xz}$, d$_{yz}$ orbitals become more stable at the small destabilization of d$_{z^2}$ orbital (in consideration of low basicity of axial ligand). For the stronger σ-donor pyridine ligand (*i.e.* 4-NH$_2$py) the destabilization of the d$_{z^2}$ orbital is too great, and formation of the six-coordinated complex at small concentration of base (up to 15-fold excess with respect of starting complex) is not observed.

A comparison of the absolute values of K_B with literature data for the low-spin Co(II) complexes reveals that the stability constants K_B for our complexes are similar to those for low-spin complexes with tetradentate Schiff bases derivatives of salicylaldehyde and diamines [16, 17], lower than the K_B constants for the complexes with derivatives of β-diketonates and diamines [18], and much lower than the values of K_B for complexes with porphyrins [11, 15, 19].

The correlations presented above (Figs. 4–6) concerning the effect of equatorial ligands indicate that a decrease in the electron density on the chelate ring is accompanied by an increase in the K_B constant. A comparison of ρ_1 and ρ_2 values obtained by us with values of reaction constant of fifth ligand attaching by low spin cobalt(II) complexes with *para* substitued tetraphenylporphyrins [11], for which the ρ constant is about seven to ten fold lower, suggest that the sensitivity to the electronic effects of substituent is much stronger in the complexes studied by us. It becomes understandable when considering the fact that initial tetrahedral complexes must transform their configuration into the squar-planar one upon coordination of the fifth ligand. In the case of the latter configuration, in consideration of the high-spin character of complex, the 'planar' orbitals *i.e.* d_{xy} and $d_{x^2-y^2}$ are half-filled and their interaction with equatorial ligand is much stronger than for low-spin complexes, where the d_{xy} orbital is empty.

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