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# EPR Studies of Solvent Coordination in Bis(dimethylglyoxime)cobalt$^{II}$ Complexes as Catalysts for Hydrogenation of Nitrobenzene

A. ROCKENBAUER, M. GYÖR

*Central Research Institute for Chemistry, Hungarian Academy of Sciences, Budapest II, Pustaszeri Ut. 59/67, Hungary*

M. KWIECIŃSKI and S. TYRLIK*

*Laboratory of Homogeneous Catalysis, Institute of Organic Chemistry, Polish Academy of Sciences, 00-961 Warsaw, Kasprzaka 44, Poland*

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*EPR spectra of diaquocobaloxime and dimorpholine cobaloxime in different solvents have been studied in frozen solutions. It has been observed that magnetic parameters for solvent complexed cobaloximes depend strongly on the nature of the solvent, whereas morpholine-complexed cobaloxime shows no substantial variation of magnetic parameters with the solvents.*

*The rates of nitrobenzene hydrogenation catalyzed by cobaloximes show considerable variation with solvent. It has been concluded that three elementary processes important for catalysis: hydrogen and nitrobenzene activation as well as hydrogen transfer, take place in the region of the active complex remote from the z axis.*

## Introduction

Catalytic properties of bis(dimethylglyoxime)-cobalt$^{II}$ as hydrogenation catalysts have recently been quite extensively studied [1–3].

The cobaloxime catalyst for nitrobenzene hydrogenation is formed according to the following reaction:

$$\mathrm{Co(dmgH)_2 2H_2O + B \xrightarrow{\text{solv.}} cat.} \quad (1)$$

where B = amine.

Hydrogenation of nitrobenzene proceeds according to the reaction:

$$\mathrm{PhNO_2 + H_2 \xrightarrow[\text{cat.}]{\text{solv.}} PhNH_2} \quad (2)$$

Some aspects of the mechanism of hydrogenation of nitrobenzene in acetone solution have been studied by EPR [4].

We recently observed that the rate of reaction (2) is strongly dependent on the nature of the solvents used. It is therefore of obvious interest to have an insight into the interaction of solvents with cobaloximes. A useful method for studying this problem is EPR.

EPR spectra of cobaloxime systems in different solvents have not been systematically studied, only scattered information existing in the literature. Schrauzer measured cobaloxime II in the presence of a excess of acetonitrile [5]. The EPR spectrum of $Co(dmgH)_2$ in methanol has been interpreted and ascribed to the dimethanol solvate $Co(dmgH)_2 \cdot 2CH_3OH$ [6]. Ivanova [7] measured $Co(dmgH)_2$ in methanol and ethanol and noted very small differences of coupling constants in these two solvents. The acetone solution of $Co(dmgH)_2 2H_2O$ shows a spectrum very similar to that of the alcohols [4].

An EPR study of reaction products of $Co(dmgH)_2$ + pyridine [6, 8, 9] pointed to the existence of 1:1 and 1:2 adducts. Their spectra were characterized and formation constants measured. Several complexes of substituted anilines and picolines with the cobaloxime moiety have also been studied by EPR [7]. It has been found that with an increase of aniline basicity the components of hyperfine coupling constants (*e.g.* $A_\parallel$, $A_\perp$) decrease.

The purpose of this paper is to study coordination of various organic solvents to the cobaloxime moiety and to obtain more information on the mechanism of catalysis.

## Experimental

### *Reagents and Solvents; Catalytic Reaction*

Diaquocobaloxime I was prepared according to Schrauzer [12]. Solvents were distilled, de-aerated and flushed with nitrogen before use. Morpholine was distilled and stored under argon.

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*Author to whom correspondence should be addressed.

TABLE I. Conditions of Recording of Spectra Shown in Fig. 1–4.

| Figure Number | | Field sweep G | Modulation G | Frequency GHz | Amplification × 100 |
|---|---|---|---|---|---|
| 1 | | 3300 ± 1000 | 6.3 | 9.2140 | 5 |
| 2 | | 3400 ± 500 | 2.0 | 9.1548 | 4 |
| 3 | a | 2700 ± 250 | 0.4 | 9.1800 | 1.8 |
| | b | 3150 ± 250 | 0.4 | 9.1800 | 1.8 |
| | c | 3580 ± 250 | 0.4 | 9.1800 | 1.8 |
| 4 | a | 3290 ± 500 | 6.3 | 9.2102 | 2.9 |
| | b | 3200 ± 500 | 2.0 | 9.2087 | 3.6 |

### *Standard Catalytic Reaction*

In a typical reaction the 100 cm$^3$ flask was flushed with argon and Co(dmgH)$_2$2H$_2$O (0.55 g, 0.0017 mol) was placed therein, under exclusion of air. Whilst flushing with hydrogen the solvent was siphoned to the flask by means of a stainless steel needle. The appropriate amount of morpholine was then added by hypodermic syringe. Finally nitrobenzene was injected. Absorption of hydrogen starts without any induction period.

### *EPR Spectra*

Solutions for spectral measurements were prepared in argon atmosphere. Transfer of solutions to the EPR tubes was performed with stainless steel needles. Spectra were recorded on the JES-ME-3X type spectrometer in X band with a field modulation of 100 kHz. Conditions at which spectra shown in figures have been obtained are given in Table I.

## Results and Discussion

### *Hydrogenation of Nitrobenzene in Different Solvents*

Twenty different solvents were used for preparation of the catalyst, according to (1) and for performing reaction (2). Rates of reaction (2) as measured by hydrogen absorption are given in Table II.

Solvents were arranged according to increasing donor number [10].

As is seen from this Table there is no catalysis in strongly coordinating solvents, probably because sites necessary for activation by coordination are occupied.

For CH$_3$NO$_2$, aromatic hydrocarbons and ethyl acetate, the reasons for inhibition are probably all different. Acidity could be responsible for the lack of catalysis in the case of nitromethane.

TABLE II. Initial Rates of Nitrobenzene Hydrogenation in Different Solvents. Catalytic system = Co(dmgH)$_2$2H$_2$O + 2 morpholine → cat. $c_{Co}$ = 40 m*M*; $c_{PhNO_2}$:$c_{Co}$ = 50; room temperature; atmospheric pressure; $V_R$ = 40 cm$^3$.

| Solvent | Initial rate of hydrogen absorption ml H$_2$/min | Donor number [10] kcal/mol |
|---|---|---|
| Hexane | 10 | – |
| Benzene | 0 | 0.1 |
| Toluene | 0 | – |
| Ethyl ether | 0 | 19.2 |
| Nitromethane | 0 | 2.7 |
| Nitrobenzene | 8 | 4.4 |
| Acetonitrile | 30 | 14.1 |
| Dioxane | 31 | 14.8 |
| Acetone | 71 | 17.0 |
| Ethyl acetate | 65 | 17.1 |
| THF | 62 | 20.0 |
| Dimethoxyethane | 48 | 24.0 |
| Methanol | 14 | 25.7 |
| DMF | 10 | 26.6 |
| DMSO | 5 | 29.8 |
| Ethanol | 5 | 31.5 |
| Pyridine | 0 | 33.1 |
| Aniline | 0 | – |
| HMPT | 0 | 38.8 |
| Water | 0 | 18.0 |

### *EPR Spectra and Coordination of Solvents to Cobaloxime Moiety*

EPR spectra of I were studied in the following solvents: Diglyme, DMF, PhCHO, PhCOCH$_3$, CH$_3$COCH$_3$, CH$_3$COOEt, CH$_2$Cl$_2$, CHCl$_3$, DMSO, are similar in character, and the spectrum typical for all the above mentioned solvents is shown in Fig. 1.

Diaquocobaloxime does not dissolve in diethyl ether, PhCOOEt, PhCH$_3$, PhNO$_2$, HCONH$_2$ to the extent which would make EPR measurement possible. Solutions of I in pyridine and aniline gives rise to the signals of dibase adducts. Rather different spectra were observed in THF and nitriles. These will be discussed later.

As is seen from Fig. 1 the well resolved region of the spectrum is a parallel part. $A_{\parallel}$ and $g_{\parallel}$ can be easily determined. Perpendicular coupling constant A has been estimated from the overall width of the

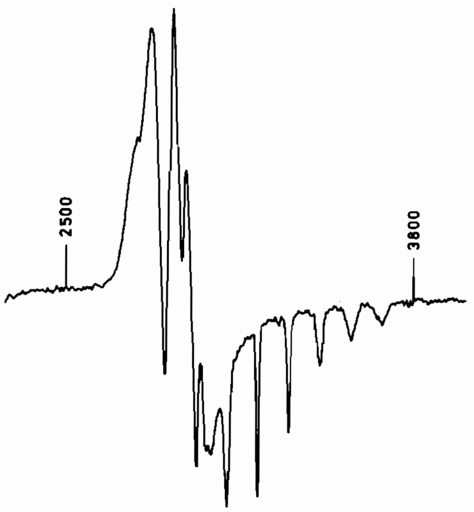

Fig. 1. EPR spectrum of the solution of I in acetophenone. Solution of saturation concentration in room temperature. Spectrum was recorded at 77 K.

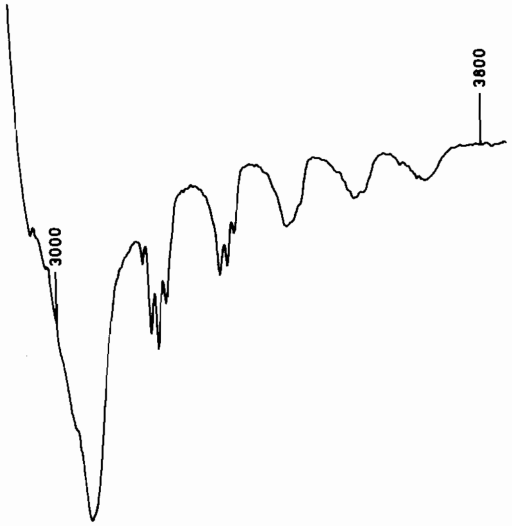

Fig. 2. EPR spectrum of the solution of I in benzonitrile. Concentration conditions and temperature of the cavity as in Fig. 1.

perpendicular part. Values of magnetic parameters for all the solvates studied, except for THF, are given in Table III.

No superhyperfine splitting was detected, except in benzonitrile.

In the latter case the parallel cobalt hyperfine lines split into 1:1:1 triplets indicating the formation of a mixed adduct with one solvent and one water molecule in the axial positions.

In all the above cases the spectra can be interpreted by assuming the presence of a single species

TABLE III. Anisotropic Coupling Constants and g Factors for Reaction Products of $Co(dmgH)_2 2H_2O$ with Different Solvents.

| Solvent | $A_{\parallel}$ G | $g_{\parallel}$ – | $A_{\perp}$ G | $g_{\perp}$ – |
|---|---|---|---|---|
| DMF | 124 | 2.015 | 46.8 | 2.39 |
| $CH_3CN$* | 125 | 2.010 | 40.5 | 2.28 |
| PhCN* | 130 | 2.014 | – | – |
| Diglime | 128 | 2.011 | – | – |
| DMSO | 118 | 2.014 | – | – |
| PhCHO | 120 | 2.015 | – | – |
| $PhCOCH_3$ | 118 | 2.016 | 38.8 | 2.27 |
| $CH_3COOEt$ | 120 | 2.012 | 37.1 | 2.25 |
| $CH_3COCH_3$ | 115 | 2.012 | 35.6 | 2.26 |
| $CH_2Cl_2$ | 116 | 2.018 | 34.0 | 2.26 |
| $CHCl_3$ | 116 | 2.016 | 33.7 | 2.26 |

*Additional triplet $A_{\parallel}^{N}$ = 16 G.

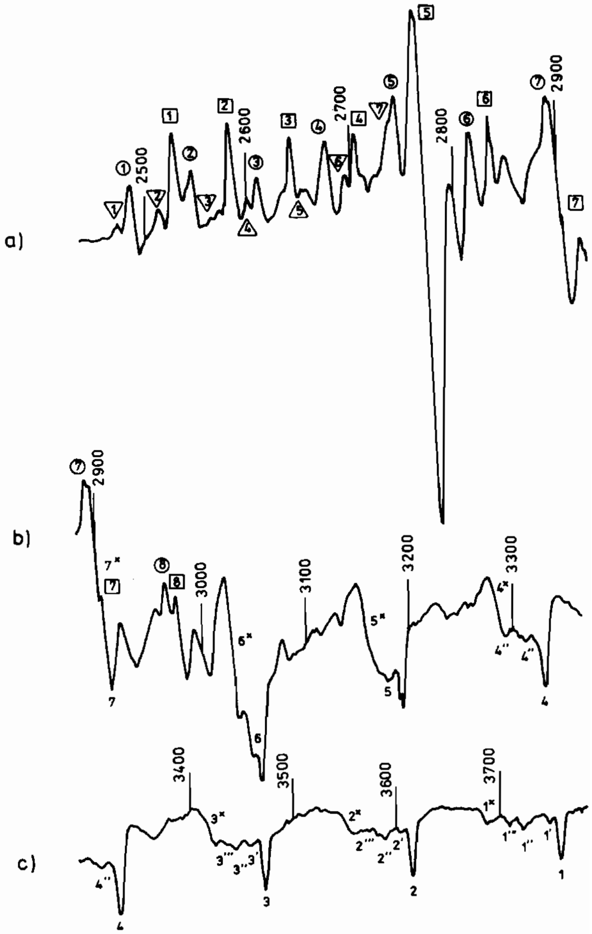

Fig. 3. EPR spectrum of the solution of I in THF. Concentration conditions and temperature as in Fig. 1. Lines described as: 1, 2, 3, ..., 1′, 2′, 3′, ..., 1″, 2″, 3″, ..., 1‴, 2‴, 3‴, ..., $1^x$, $2^x$, $3^x$, ..., correspond to the parallel cobalt hyperfine splitting of individual components of solution. Lines depicted as: ▽, ▽, ▽, ..., ①, ②, ③, ..., $\boxed{1}$, $\boxed{2}$, $\boxed{3}$, ..., correspond to the perpendicular cobalt hyperfine splitting of the same components.

TABLE IV. Anisotropic Coupling Constants and g Factors of Two Reaction Products of $Co(dmgH)_2 2H_2O$ with THF.

| Reaction | $A_{\parallel}$ G | $g_{\parallel}$ – | $A_{\perp}$ G | $g_{\perp}$ – |
|---|---|---|---|---|
| 1) Component of the solution showing lines depicted as $\boxed{1}$, $\boxed{2}$, ... in the low field region and as 1, 2 in the high field | 139 | 2.0150 | 64.2 | 2.400 |
| 2) Component showing lines depicted as ①, ②, ... in the low field region and as $1^x$, $2^x$, ... in the high field | 129 | 2.0370 | 68.5 | 2.4240 |

in the solvent. In THF, however, a complex spectrum was observed, where lines from five different species can be distinguished.

In Table IV the magnetic parameters of the two most intensive components are given.

Formation of more than one species in THF is understandable when one considers the strong donor properties of this solvent.

For instance, THF affects the visible spectrum of disodium benzophenone [11] in the most pronounced way from all the monoethers. Gutman stressed [10] that the donor number for THF is the largest among all the monoethers. One can therefore expect that THF will form complexes with weak Lewis centres in the coordination compound, which do not coordinate with other etheral donors. One can expect existence of several such centres in cobaloximes: not only the $d_{z^2}$ orbital usually occupied by $\sigma$ donors but also $d_{x^2}$ and $d_{yz}$ orbitals. Interaction of THF with OHO in plane bridge also could not be excluded. These interactions will give rise to several EPR active species in THF solution.

### *Coordination of Morpholine to the Co(dmgH)$_2$ Unit in Different Solvents*

Reactions of morpholine with diaquocobaloxime:

$$Co(dmgH)_2 2H_2O + MR \xrightarrow{\text{solv.}} Co(dmgH)_2 2MR \qquad (3)$$

were performed in the molar ratio Co:MR = 1:7. In this molar ratio we expected an exclusive formation of 1:2 complex, and not a mixture of 1:1 and 1:2 complexes. This is based on the polarographic measurements of stability constants of 1:1 and 1:2 complexes in DMSO with 11 different amines [14]. DMSO is a rather strongly-coordinating solvent compared with the solvents listed in Table II.

As the stability constant for the monomorpholine complex is 190 and for dimorpholine 62, and as the concentration of the former is dependent on [B] and the latter on $[B]^2$, the above-mentioned assumption is justified.

All observed spectra, except in benzaldehyde, were of the same type (Fig. 4).

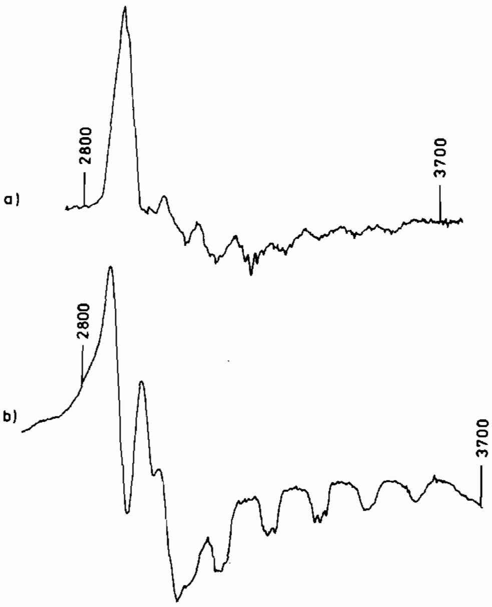

Fig. 4. a) EPR spectrum of the reaction product of diaquocobaloxime with morpholine in molar ratio 1:7 in acetophenone. Cobalt concentration (at room temperature) 50 m*M*. Temperature of the cavity 77 K. b) EPR spectrum of the reaction product I + morpholine in benzaldehyde.

While in the parallel part we can observe a well resolved structure, in the perpendicular part of the spectrum the pattern merges into a singlet. Some of the parallel lines are further split by interaction with two axial nitrogens, which give rise to 1:2:3:2:1 pattern.

The only exception is the spectrum in PhCHO where a 1:1:1 pattern arises. This indicates formation

TABLE V. Anisotropic Coupling Constants and g Values for Dimorpholine Adducts in Different Solvents.

| Solvent | $A_{\parallel}$ G | $g_{\parallel}$ – | $A_{\parallel}^{N}$ G |
|---|---|---|---|
| PhCN | 96.1 | 2.28 | 16.0 |
| Diglime | 96.0 | 2.29 | 14.2 |
| PhCOOEt | 94.3 | 2.27 | 15.6 |
| $PhCH_3$ | 92.3 | 2.27 | 15.2 |
| $PhNO_2$ | 94.2 | 2.26 | 15.5 |
| $CH_3COOEt$ | 92.2 | 2.26 | 15.4 |
| DMSO | 92.2 | 2.27 | 14.8 |
| DMF | 92.2 | 2.28 | 15.8 |
| $CH_3CN$ | 92.2 | 2.25 | 16.0 |
| $PhCOCH_3$ | 90.1 | 2.27 | 14.9 |
| $CH_3COCH_3$ | 88.4 | 2.27 | 13.9 |
| $CH_2Cl_2$ | 88.3 | 2.28 | 14.8 |
| $CHCl_3$ | 88.2 | 2.29 | 15.1 |
| $HCONH_2$ | 88.2 | 2.27 | 14.5 |

of $Co(dmgH)_2MR \cdot PhCHO$ complex. In all the other solvents dimorpholine adducts $Co(dmgH)_2 2MR$ are formed. Magnetic parameters for these complexes are given in Table V.

### *Discussion of Fermi Constant and Orbital Reduction Parameters*

Parameters of hyperfine interaction for cobalt complexes can be expressed by the following equations [12]:

$$A_{\parallel} = -K + \frac{P}{7}(4k'^2 - \Delta g_{\perp}) \tag{4}$$

$$A_{\perp} = -K + \frac{P}{7}\left(-2k'^2 - \frac{15}{2}\Delta g_{\parallel}\right) \tag{5}$$

where:

$\Delta g_{\perp} = g_{\perp} - 2.0023$; $P = g_o g_N \mu_B \mu_N \langle r^{-3} \rangle = 235$ G; $g_o = 2.0023$; $g_N$ = nuclear factor for $Co^{59}$; $\mu_B$ and $\mu_N$ are electron and nuclear magnetons; r = an average distance between the unpaired electron and the cobalt nucleus; K = Fermi constant; k′ = orbital reduction parameter.

In this formalism the variation of hyperfine constants is described by the latter two parameters. Table VI summarizes the magnetic parameters and K, $k'^2$ constants for the complexes studied.

Complexes are arranged here according to their magnetic parameters as well as K and $k'^2$. It can be seen that the orbital reduction parameter varies in the opposite direction from the algebraic value of the Fermi constant. This correlation can be explained in terms of the ligand field theory: the more covalent the axial $\sigma$ bond, *i.e.* the smaller is $k'^2$, the smaller the deviation that can be expected from the octahedral symmetry around the $Co^{II}$ ion. The small distortion in turn leads to a smaller $3d_{z^2}-4s$ mixing and therefore a smaller negative contribution of K because the 4s spin population is smaller.

In this context we suggest a very weak axial bonding in the case of THF, where K $\cong$ −60 G and $k'^2 \cong 0.9$ and a strong axial $\sigma$ bond in the presence of MR where K is around −20G and $k'^2 \cong 0.8$. In all the other cases the covalency of axial $\sigma$ bond has an intermediate value.

An interesting case is $Co(dmgH)_2MR \cdot PhCHO$ where only one morpholine coordinates to cobalt and the axial position is occupied by the solvent molecule.

The Fermi constant is −36 and the orbital reduction parameter 0.79. The low value of $k'^2$ suggests strong $\sigma$ bonding, but the intermediate value of K indicates considerable distortion from octahedral symmetry. The same has been observed for the $Co(dmgH)_2Py$ 5-coordinate and $Co(dmgH)_2 2Py$ 6-coordinate complexes [6]. The relatively large distortion from octahedral symmetry when one base is coordinated to cobalt may be explained by the displacement of the cobalt atom relative to the plane of the dmgH ligands. $A_N$ for $Co(dmgH)_2MR \cdot PhCHO$

TABLE VI. Anisotropic Coupling Constants, g Values, Fermi Constants and Orbital Reduction Parameters for Complexes of $Co(dmgH)_2$ Unit.

| Complex of $Co(dmgH)_2$ unit | $A_{\parallel}$ G | $A_{\perp}$ G | $g_{\perp}$ – | K G | $k'^2$ – |
|---|---|---|---|---|---|
| THF solutions | 130–140 | 64–68 | 2.40 | −62–−59 | 0.92–0.88 |
| All other solvents, nitrile included | 125–130 | 35 | 2.26 | −48 | 0.83 |
|  | 120 | 30–35 | 2.26 | −44 | 0.82 |
|  | 115–120 | 30 | 2.26 | −41 | 0.80 |
| $Co(dmgH)_2 \cdot MR \cdot PhCHO$* | 110 | 25 | 2.70 | −36 | 0.79 |
| Dimorpholine complexes $Co(dmgH)_2 \cdot 2MR$ | 88–96 | 13 | 2.70 | −21 | 0.77 |

*$A^N$ for this complex is 14 G.

is almost identical to the $A_N$ in the $Co(dmgH)_2 2MR$ complex, suggesting quite strong $\sigma$ axial bonds between the central cobalt and morpholine in both cases. It indicates that once the first axial nitrogen–cobalt bond is formed it is slightly influenced by what is going on in the second axial position.

### *Comment on the Influence of Solvents on the Rate of Catalytic Reaction*

For $Co(dmgH)_2 2MR$ in different solvents we observed a rather minor variation of magnetic parameters (Table VI). In the light of what was discussed in the preceding section one can expect the same for $Co(dmgH)_2 MR$. It signifies that solvents influence very slightly the electron densities in the region of the complex which lies along the $z$ axis, provided that the first morpholine molecule has been coordinated to cobalt atom.

On the other hand, as follows from Table II the rate of reaction (2) is strongly solvent dependent. Reaction (2) is undoubtedly a multistep process. These steps consist of: activation of hydrogen, activation of nitrobenzene, transfer of the first hydrogen molecule with the subsequent formation of the first intermediate and eventually transfer of remaining hydrogen molecules.

As the kinetic study indicates [15], the transfer of the first $H_2$ is a rate limiting step and takes place intermolecularly within a binuclear, nitrobenzene complexed cobaloxime:

$$[HCo(dmgH_2)(dmgH)B]_2 \cdots PhNO_2 \longrightarrow 2Co(dmgH)_2B + \text{very first product of nitrobenzene reduction} \qquad (6)$$

Solvents influence electron densities in the region of the complex lying along the $z$ axis very slightly, but have strong influence on the rate of the catalytic reaction. The EPR result is, therefore, in agreement with kinetic study, showing that hydrogen activation reaction gives rise to $HCo(dmgH_2)(dmgH)B$, the nitrobenzene activation process produces

$$[HCo(dmgH_2)(dmgH)B]_2 \cdots PhNO_2,$$

as well as hydrogen transfer takes place within an intermediate shown in Fig. 5.

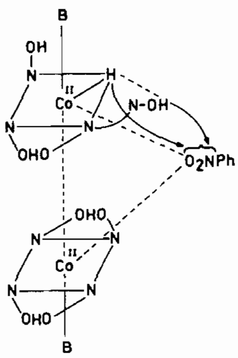

Fig. 5. Mode of hydrogen activation and transfer in nitrobenzene complexed dimeric cobaloxime.

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