

# Solvation of Coordinatively Saturated Metal Complexes of Nitrogen Ligands

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$^1\text{H}$  NMR shifts were measured for ten organic compounds *L* in solutions containing paramagnetic bis[hydrotris(1-pyrazolyl)borato]cobalt(II),  $\text{Co}(\text{HBpz}_3)_2$ . The observed paramagnetic shifts were accounted for by pseudo-contact interactions in the outer-sphere adducts of  $\text{Co}(\text{HBpz}_3)_2 \cdot L$ . From the concentration dependence of the induced shifts, the thermodynamic parameters of the outer-sphere complexation were determined. It is shown that a simple electrostatic model of  $\text{Co}(\text{HBpz}_3)_2$  solvation is not consistent with the experimental results. Comparison of the data for pyrazolylborate and  $\beta$ -diketonate transition metal complexes showed that the specificity of the outer-sphere solvation depends to a large extent on the nature of the first coordination sphere ligands.  $\text{Co}(\text{HBpz}_3)_2$  induces anomalous shifts of the signals of NMR standards. It is necessary to assume a specific interaction between the standards and  $\text{Co}(\text{HBpz}_3)_2$ .

## Introduction

Studies dealing with the second coordination sphere of neutral transition metal complexes in solutions are of great importance because the composition and the thermodynamic and kinetic stability of these compounds are determined in some cases by outer-sphere solvation effects (see review [1]). In a series of papers by Eaton et al. [2–4] the structure of the second coordination sphere has been studied by  $^1\text{H}$  NMR spectroscopy. The paramagnetic complex bis[hydrotris(1-pyrazolyl)borato]cobalt(II) (*M*) having a very large magnetic anisotropy ( $g_{\parallel} = 8.46$ ,  $g_{\perp} = 0.95$  [5]), it was the object of the investigations (Figure 1). Pseudo-contact shifts of proton signals from organic solvents oriented in the outer-sphere of *M* are described by

$$\Delta\delta_{\text{pc}} = D(3\cos^2\theta - 1)r^{-3}(g_{\parallel}^2 - g_{\perp}^2), \quad (1)$$

where  $r$  is the distance between the metal atom and the nucleus under consideration,  $\theta$  the angle between the principle axis of the molecule and the vector from the metal atom to the ligand nucleus, and  $D$  a constant which depends on the relative values of the electron relaxation time, the Zeeman anisotropy energy, and the correlation time for molecular tumbling [6]. In [2–4] the *M*-induced paramagnetic shifts were used to draw the following

conclusions: (1) The outer-sphere coordination of the solvent takes place in the plane perpendicular to the symmetry axis of the complex ( $\theta = 90^\circ$ ) and the solvent molecules are oriented with the positive end towards the metal (Fig. 1a) and (2) the outer-sphere interactions are Coulombic in nature.

Recently new methods appeared which allowed for a reliable evaluation of the thermodynamic parameters of the outer-sphere complexation. The methods are based on concentration dependence studies of NMR parameters of the outer-sphere ligands of paramagnetic metal complexes in inert solvents. The majority of the investigations was

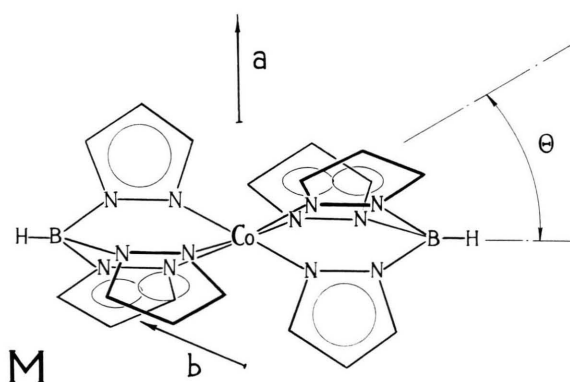


Fig. 1. Structure of  $\text{Co}(\text{HBpz}_3)_2$  and possible preferable orientations of the outer-sphere ligands. Solvating molecules are depicted by arrows directed from their positive to their negative end.

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carried out on  $\beta$ -diketonates of transition metals [1]. We therefore decided to evaluate the thermodynamic parameters of outer-sphere adducts of M type complexes of nitrogen ligands, hoping to get new information about outer-sphere solvation.

## Experimental

$\text{Co}(\text{HBpz}_3)_2$  and  $\text{Ni}(\text{HBpz}_3)_2$  complexes were synthesized by the method of Trofimenko [7]. The NMR spectra were obtained on a Bruker SXP-4-100 spectrometer. The  $\text{C}_6\text{H}_5\text{NO}_2 + \text{M}$  system was studied on a Bruker WM-400 spectrometer. All the experiments were carried out at ambient temperature with the exception of the enthalpy and entropy studies, where the temperature varied from  $0^\circ$  to  $67^\circ\text{C}$ . TMS was used as an internal standard.

On addition of  $\text{Co}(\text{HBpz}_3)_2$ , the  $^1\text{H}$  NMR signals of various organic solvents experience upfield shifts proportional to the complex concentration. In all cases the shifts induced by  $\text{Co}(\text{HBpz}_3)_2$ ,  $\Delta\delta$ , are much larger than those induced by  $\text{Ni}(\text{HBpz}_3)_2$ , which underlines their pseudo-contact nature (one should expect that  $\text{Ni}(\text{II})$  octahedral complexes have no pseudo-contact component in the isotropic shift [8]). A confirmation of the pseudo-contact mechanism of the  $\text{Co}(\text{HBpz}_3)_2$ -induced NMR shifts was obtained from investigations of  $^{13}\text{C}$  NMR spectra. In all cases  $\Delta\delta(^1\text{H}) \gg \Delta\delta(^{13}\text{C})$  was found. For contact NMR shifts of outer-sphere ligands one should expect  $\Delta\delta(^1\text{H}) \ll \Delta\delta(^{13}\text{C})$  ([1] and references therein).

If L molecules exchange quickly between the complex solvate shell and the bulk solvent, the observed change of solvent NMR chemical shift induced by the metal complex,  $\Delta\delta$ , depends on the fraction of coordinated L molecules,  $p_L$ , and on the shift induced directly in the outer sphere,  $\Delta\delta^0$ :

$$\Delta\delta = p_L \Delta\delta^0.$$

Within the limits of a trivial one-step complexation scheme  $\text{M} + \text{L} \rightleftharpoons \text{M}^*\text{L}$  the observed shifts will be determined by the relationship [9]

$$\Delta\delta = \Delta\delta^0 [\text{M}]_0 K_{\text{eff}} / (1 + K_{\text{eff}} [\text{L}]_0), \quad (2)$$

where  $K_{\text{eff}}$  is the effective equilibrium constant,  $[\text{M}]_0$  and  $[\text{L}]_0$  are the initial concentrations of M and L, and  $[\text{M}]_0 \ll [\text{L}]_0$ . One can evaluate  $K_{\text{eff}}$  and  $\Delta\delta^0$  analyzing the dependence of  $\Delta\delta$  on L concentration

in an inert solvent S with the help of (2) if  $[\text{L}]_0$  is small ( $[\text{L}]_0 < 1.5 \text{ M}$ ) [9]. If a single complex molecule has several equivalent outer-sphere coordination centers,  $K_{\text{eff}}$  is equal to the equilibrium constant of the outer-sphere complex formation with each of these centers [1].

When trying to experimentally evaluate  $K_{\text{eff}}$ , the choice of an "inert" solvent S is crucial [9]. We used carbon tetrachloride, because it readily dissolves pyrazolylborate complexes. It should be noted that the solubility of metal complexes in  $\text{CCl}_4$  itself proves the interaction between M and S [10]. It has been shown earlier that  $\text{CCl}_4$  interacts with transition metal  $\beta$ -diketonates [11, 12]. One can assume that the same effect exists for pyrazolylborates. The interaction  $\text{M} + \text{S} \rightleftharpoons \text{M}^*\text{S}$  reduces the observed  $K_{\text{eff}}$  values, but still the values allow to compare the outer-sphere coordination ability of L compounds [9]. It is impossible to use saturated hydrocarbons as S (as it was done in the case of  $\beta$ -diketonates [9]) because of too low pyrazolylborates' solubility.

Some typical plots of the observed  $\text{Co}(\text{HBpz}_3)_2$ -induced  $^1\text{H}$  NMR shifts vs.  $[\text{L}]_0$  are shown in Figure 2. The values of  $K_{\text{eff}}$  and  $\Delta\delta^0$  calculated on the basis of the concentration dependence of the  $\Delta\delta$  shifts are found in Table 1. If a molecule has several groups of equivalent protons, the  $\Delta\delta_{\text{max}}^0$  values for the protons with maximal shifts as well as the  $\Delta\delta^0$  ratios for all the groups are tabulated. All the

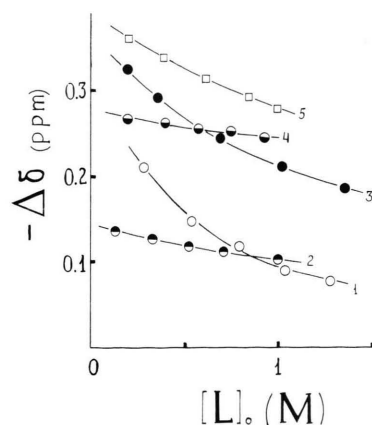


Fig. 2. Concentration dependence of induced shifts in systems  $\text{L} + \text{CCl}_4 + \text{TMS}$  (3% v/v) +  $\text{Co}(\text{HBpz}_3)_2$ :

L = DMSO,	$[\text{M}]_0 = 7.73 \cdot 10^{-2} \text{ M}$ (1);
L = acetone,	$[\text{M}]_0 = 8.61 \cdot 10^{-2} \text{ M}$ (2);
L = acetonitrile,	$[\text{M}]_0 = 6.22 \cdot 10^{-2} \text{ M}$ (3);
L = 4-methylpyridine,	$[\text{M}]_0 = 8.14 \cdot 10^{-2} \text{ M}$ (4);
L = 4-nitrotoluene,	$[\text{M}]_0 = 5.78 \cdot 10^{-2} \text{ M}$ (5).

tabulated parameters are the results of averaging 3–4 independent series of experiments. The experimental errors were 10–25%, depending on the system investigated.

## Results and Discussion

### Geometry and Nature of $\text{Co}(\text{HBpz}_3)_2 \cdot \text{L}$ Adducts

For all the outer-sphere ligands with several proton groups maximal shifts are observed for the protons situated near the positive end of the molecular dipole, and one would think that this fact is consistent with the solvation model suggested by Eaton [2] (Figure 1a). It seems to us, however, that an inspection of Table 1 allows to propose another version. If the outer-sphere ligands were located in the equatorial plane of M (the angle  $\theta$  for all L nuclei approaching  $90^\circ$ ) then  $\Delta\delta_{\text{pc}}$  in (1) should depend only on the distance  $r$ , and the shifts  $\Delta\delta^0$  should be related to each other as  $1/r^3$ . No rigorous mathematical analysis is necessary to state that this is not correct neither for 4-nitroanisole nor for 4-nitrotoluene or 4-methylpyridine. It is obvious, for example, that for the H-2 and H-3 protons of 4-nitrotoluene (or 4-nitroanisole) the parameters  $1/r^3$  must differ much less than for the H-2 and methyl protons. The  $\Delta\delta^0$  shifts listed in Table 1 exhibit, however, opposite trends. Even if one

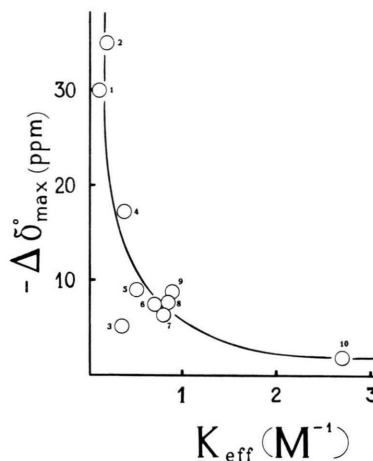


Fig. 3. Plot of  $\Delta\delta_{\text{max}}^0$  vs.  $K_{\text{eff}}$ . Numbering of points as in Table 1.

proposes that the shifts  $\Delta\delta^0$  may depend on the distance as  $r^{-4}$  due to the lability of outer-sphere structure [2], this fact would not explain the pattern of the induced shifts' distribution.

Moreover, it is natural to expect that, as the stability of the outer-sphere adducts increases, the distance between the interacting molecules decreases. If the outer-sphere coordination is as in Fig. 1a, the increase of  $K_{\text{eff}}$  would be followed by an increase of the shifts' absolute values (see (1)). However, in Fig. 3, where  $\Delta\delta_{\text{max}}^0$  is plotted against  $K_{\text{eff}}$ , one can see an reverse trend, i.e. the shift diminishes as the stability of adducts increases. One of the possible explanations of this effect might be the decrease of the magnetic anisotropy of M on solvation. In this case one can expect, however, that the NMR shifts for the protons of inner-sphere ligands of M, for which the pseudo-contact contribution is large [13], should strongly vary upon addition of L. Appropriate experiments showed that the chemical shifts for the four signals of the inner-sphere  $\text{Co}(\text{HBpz}_3)_2$  ligands did not depend on the solvent (variations were less than 3%). This confirms the constancy of the magnetic anisotropy.

The observed effects can be easily explained if one supposes the outer-sphere coordination sites to be located at the periphery of M in the region of the pyrazole rings or boron atoms (see Figure 1b). In this case it is necessary to take into account not only the  $\Delta\delta^0$  dependence on  $r$  but also its dependence on  $\theta$ . Thus, for the nuclei being in the vicinity of a cone  $\theta_0 \cong 55^\circ$  ( $3 \cos^2 \theta_0 = 1$ ) the pseudo-contact

Table 1. Stability constants and paramagnetic shifts for the M · L adducts.

Nr.	L	$K_{\text{eff}}$ ( $\text{M}^{-1}$ )	$-\Delta\delta_{\text{max}}^0$ (ppm) <sup>a</sup>	The shifts ratio
1	4-Methylpyridine	0.11	30.0	H-2:H-3:Me = -10:+15:+30
2	Nitrobenzene	0.19	35.1	H-2:H-3:H-4 = 8:24:35
3	Acetone	0.37	4.9	
4	4-Nitrotoluene <sup>b</sup>	0.39	17.2	H-3:H-2:Me = 0:13:17
5	Nitromethane	0.51	8.9	
6	Propionitrile <sup>c</sup>	0.71	7.2	$H_\alpha:H_\beta = 4.4:7.2$
7	Butyronitrile <sup>d</sup>	0.80	6.0	$H_\alpha:H_\beta:H_\gamma = 3.6:5.6:6.0$
8	Acetonitrile	0.85	7.5	
9	4-Nitroanisole <sup>e</sup>	0.89	8.6	H-3:H-2:Me = 1.4:5.9:8.6
10	DMSO	2.7	1.7	

<sup>a</sup> Downfield shifts are taken to be positive.

<sup>b</sup> Methyl is in position 1. — <sup>c</sup>  $\text{N} \equiv \text{C}-\text{C}^2\text{H}_2-\text{C}^3\text{H}_3$ .

<sup>d</sup>  $\text{N} \equiv \text{C}-\text{C}^2\text{H}_2-\text{C}^3\text{H}_2-\text{C}^4\text{H}_3$ .

<sup>e</sup> Methoxy group is in position 1.

shifts will be close to zero even if the  $r$  distances are small. The analysis of the molecular structure of M [14] shows that the cone  $\theta_0 \cong 55^\circ$  crosses pyrazole rings. If the outer-sphere coordination sites are situated near this cone, the angles  $\theta$  for L can approach  $\theta_0$  and the shifts  $\Delta\delta^0$  can decrease with increase of the stability of the outer-sphere adducts in accordance with Figure 3. In this case the downfield shift for the 4-methylpyridine H-2 protons may be due to the location of part of an outer-sphere L molecule within the cone  $\theta_0 \cong 55^\circ$ . Within the limits of the suggested model, maximal shifts for the protons situated near the positive ends of molecular dipoles may be explained by the relative proximity of these protons to the plane  $\theta = 90^\circ$  rather than by their proximity to the metal atom (Figure 1b).

The question arises whether an L molecule interacts with the metal complex as an indivisible dipole or if the outer-sphere coordination of L is based on the interaction of parts of it. To answer this question it is useful to compare the stability of M–L adducts with the dipole moments  $\mu$ (L). A plot of  $\ln K_{\text{eff}}$  vs.  $\mu$  is shown in Figure 4. As it is seen, the linear correlation expected for the nonspecific electrostatic interaction is very poor (correlation coefficient 0.45). Within the limits of the electrostatic model the lack of correlation may be explained if the L molecule is regarded as a system of point charges. It means that not only the total dipole moment of the molecule is important but also the distribution of

atomic charges within the molecule. Thus, the special stability of DMSO adducts may be accounted for by a high degree of S=O bond polarization that results in the appearance of large noncompensated charges on the S and O atoms [15].

One can offer an alternative explanation of the observed  $\ln K_{\text{eff}}$  vs.  $\mu$  spread of points. It is based on the assumption of specific M–L donor-acceptor outer-sphere interactions. For example, a possible reason for peculiar stability of DMSO–M adducts may be the simultaneous formation of two outer-sphere bonds by each DMSO molecule. These bonds may be formed via an S=O fragment and a methyl group or via the two methyl groups (donor-acceptor bond formation with methyl fragments of organic molecules was shown in [16]). In this case one may regard the DMSO–M adducts as a kind of "chelate" outer-sphere complexes.

Partial transfer of spin density from a metal complex to outer-sphere ligand carbon atoms might prove donor-acceptor interactions [16]. However,  $^{13}\text{C}$  NMR experiments failed to detect such a transfer. Unlike the case of paramagnetic  $\beta$ -diketonates [16],  $^{13}\text{C}$  contact shifts of outer-sphere ligands were found neither for  $\text{Co}(\text{HBz}_3)_2$  nor for  $\text{Ni}(\text{HBpz}_3)_2$ . The absence of the spin density transfer from M to L does not exclude, however, the possibility of outer-sphere donor-acceptor bond formation, and the question of the relative importance of electrostatic and donor-acceptor interactions in the energetic balance of the outer-sphere complexation still remains open.

Finally, it is worth mentioning that the  $K_{\text{eff}}$  values for acetonitrile, propionitrile and butyronitrile are similar. The dipole moments of these compounds are also similar, and they are determined mainly by the polarization of fragment  $\text{C}-\text{C}\equiv\text{N}$  which is the negative end of the molecular dipole. If one assumes that the nitrile coordination occurs via the positive dipole end, the  $K_{\text{eff}}$  should diminish in the following sequence  $\text{MeCN} > \text{EtCN} > \text{PrCN}$  because the distance from M to a polarized fragment L grows. On the contrary, if the CN group participates in the nitrile outer-sphere coordination, the stability of the adducts formed should be similar. This assumption is in agreement with the experimental results.

So, the above results are in evident disagreement with the model of outer-sphere solvation proposed by Eaton. On the basis of the data obtained one can conclude that outer-sphere coordination of

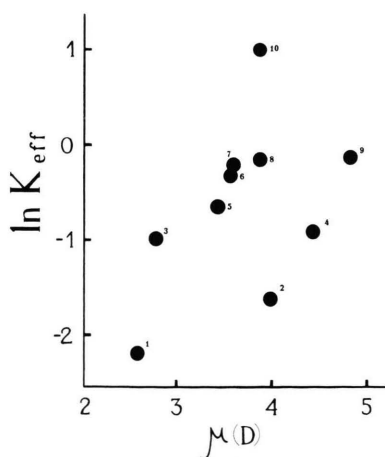


Fig. 4. Plot of  $\ln K_{\text{eff}}$  vs. dipole moment  $\mu$ . Numbering of points as in Table 1.



$\text{Co}(\text{HBpz}_3)_2$  is realized as is schematically shown in Figure 1b. The nature of the outer-sphere interactions is not yet absolutely clear. But it is obvious that a simple dipole-dipole electrostatic model can not explain the experimental effects.

For a number of organic compounds the stability of the outer-sphere adducts  $L$  with  $M$  is too low and  $K_{\text{eff}}$  cannot be evaluated on the basis of the concentration dependence (estimation shows that  $K_{\text{eff}} < 0.1 \text{ M}^{-1}$  in this case). At the same time the observed induced shifts show that these solvents do interact with  $M$ . Even without estimation of the  $K_{\text{eff}}$  values one can obtain a comparative stability series for the  $M-L'$  adducts. To solve this problem we studied induced shifts  $\Delta\delta$  in binary solutions  $L'_1-L'_2$  as a function of the mixture composition, the concentration of  $M$  being constant. If compound  $L'_1$  interacts with  $M$  more strongly than  $L'_2$ , a relative increase of the concentration of  $L'_1$  should result in a decrease of the shifts for both  $L'_1$  and  $L'_2$  [17]. Having utilized this method we obtain the following stability series for  $M \cdot L': L' = \text{pyridine} > \text{benzene} \cong \text{toluene} \cong \text{anisole} \cong \text{CH}_3\text{I} \cong \text{C}_2\text{H}_5\text{I} > \text{CH}_2\text{ClCH}_2\text{Cl} \cong \text{CHCl}_2 - \text{CH}_3 > \text{CH}_2\text{Cl}_2 \gtrsim \text{CH}_3 - \text{CCl}_2 \simeq \text{CHCl}_3 > \text{CCl}_4$ .

It is interesting to compare the outer-sphere complexation for pyrazolylborate and  $\beta$ -diketotatanate complexes. Thermodynamic parameters for the solvation of tris(acetylacetonate)chromium(III) ( $\text{Cr}(\text{acac})_3$ ) have been obtained earlier for a large number of organic solvents [9]. Using the method described in [9] we determined the stability constant for the  $\text{Cr}(\text{acac})_3 \cdot \text{DMSO}$  complex ( $K_{\text{eff}} = 0.35 \text{ M}^{-1}$ ) and the spin-lattice relaxation rate for the DMSO protons in the solvation shell of  $\text{Cr}(\text{acac})_3$  ( $R_1^0 = 6.35 \text{ kHz}$ ).  $\text{Co}(\text{HBpz}_3)_2$  and  $\text{Cr}(\text{acac})_3$  have similar structural features: both of them are neutral, stable and both have no vacant coordination sites, for in both the central ion is surrounded by six equivalent donor atoms. But the stability series of the outer-sphere adducts for the two complexes differ. This is mainly due to the fact that the  $\text{Cr}(\text{acac})_3$  oxygen atoms have lone pairs, participating in the formation of hydrogen bonds with the solvent molecules, while  $\text{Co}(\text{HBpz}_3)_2$  has no such pairs. Thus, proton-donor solvents effectively solvate  $\text{Cr}(\text{acac})_3$  but in the case of  $\text{Co}(\text{HBpz}_3)_2$ , as it was mentioned earlier [4] and as it is supported by our results, they do not compare to other solvents.

There are some more differences in the solvation series for  $\text{Cr}(\text{acac})_3$  and  $\text{Co}(\text{HBpz}_3)_2$ . The most

peculiar one is the difference in the stabilities of their adducts with DMSO. In the case of  $\text{Co}(\text{HBpz}_3)_2$ , DMSO forms more stable adducts than any other compound studied, but in the case of  $\text{Cr}(\text{acac})_3$  DMSO forms adducts with relatively low stability (even as compared with solvents that are not proton donors). The data obtained show that the outer-sphere solvation specificity is based not only on the nature of the outer-sphere ligands but also that of the first coordination sphere ligands.

For more complete characterization of outer-sphere adducts it is desirable to know the enthalpies and entropies of their formation. These parameters may be obtained from the temperature dependence of  $K_{\text{eff}}$ . For  $\text{Co}(\text{HBpz}_3)_2$  complexes of DMSO, acetonitrile and nitromethane  $\Delta H$  are  $-3.5 \pm 0.5$ ,  $-2.6 \pm 0.6$  and  $-2.3 \pm 0.6 \text{ kcal mole}^{-1}$ , and  $\Delta S$  are  $-9.7 \pm 2.0$ ,  $-9.0 \pm 2.4$  and  $-9.0 \pm 2.5 \text{ cal mole}^{-1} \text{ K}^{-1}$  respectively. These values are within the characteristic ranges of the parameters for  $\text{Cr}(\text{acac})_3$  outer-sphere adducts [9]. It is natural that the outer-sphere adducts with such weak interactions cannot be treated as static systems with fixed bond lengths and with fixed mutual orientation of the partners [2].

#### *$\text{Co}(\text{HBpz}_3)_2$ Interactions with Reference Compounds*

In NMR experiments with paramagnetic systems it is desirable to use internal standards. This makes a correction for a change in the bulk susceptibility unnecessary. The correction in the case of paramagnetic solutions may be much larger than the observed fine effects of specific solvation, and a reasonable account of such correction factor is very difficult, especially in the case of magnetically anisotropic complexes. Originally, we intended to use any of three widely used compounds (tetramethylsilane, hexamethyldisiloxane, cyclohexane) as an internal standard. But our experiments revealed an unusual effect: addition of  $\text{Co}(\text{HBpz}_3)_2$  to a solution results in a change of the mutual shift for any given pair of standards  $E$  and  $E'$  and this change,  $\Delta\delta(E, E')$ , is proportional to the  $M$  concentration. In the presence of  $M$  the cyclohexane signal shifts to a higher field and the HMDS signal shifts to a lower field relative to the conditionally "fixed" TMS signal. The induced shifts at  $[M]_0 = 0.1 \text{ M}$  in methylenechloride for cyclohexane and HMDS are  $-0.05 \text{ ppm}$  and  $+0.05 \text{ ppm}$ , respectively. In the case of  $\text{Ni}(\text{HBpz}_3)_2$ , the shifts  $\Delta\delta(E, E')$  are much

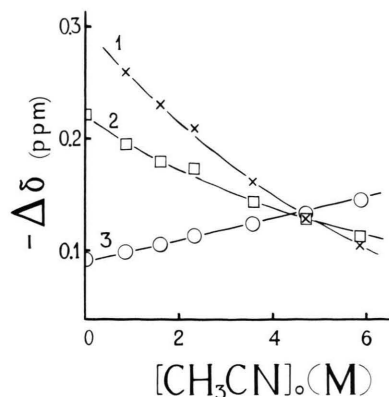


Fig. 5. Concentration dependence of induced shifts in the system  $\text{CH}_3\text{CN} + \text{CH}_2\text{Cl}_2$  (3% v/v) +  $\text{C}_6\text{H}_{12}$  (3% v/v) + HMDS (3% v/v) +  $\text{Co}(\text{HBpz}_3)_2$  (0.1 M):  $\text{CH}_3\text{CN}$  (1);  $\text{CH}_2\text{Cl}_2$  (2);  $\text{C}_6\text{H}_{12}$  (3).

smaller, which is in accordance with their pseudo-contact nature.

A characteristic property of the  $\Delta\delta(E, E')$  shifts is their increase as the solvation ability of a solvent increases. Thus for  $\text{CH}_2\text{Cl}_2$  the values of  $\Delta\delta(E, E')$  are twice those for  $\text{CCl}_4$ . On addition of L solvents with a high solvation ability to methylenechloride the  $\Delta\delta(E, E')$  shifts increase for given M concentration. As an example, the concentration dependence of induced paramagnetic shifts (relative to HMDS) in acetonitrile + methylenechloride + cyclohexane + HMDS + M is presented in Figure 5. An increase of  $[\text{CH}_3\text{CN}]_0$  results in a decrease of the  $\text{CH}_3\text{CN}$  and  $\text{CH}_2\text{Cl}_2$  shifts and in an increase of the cyclohexane shift. At  $[\text{CH}_3\text{CN}]_0 \sim 5$  M the cyclohexane shift becomes larger than the shifts for all other solvent components.

Due to the unusual properties of the standard compounds, correct measurements of induced shifts become problematic. As it was noted we used TMS as an internal standard when measuring the paramagnetic shifts  $\Delta\delta$ . Special experiments showed that substitution of TMS by HMDS or cyclohexane caused only minor changes in  $K_{\text{eff}}$  and  $\Delta\delta^0$  (of the order of the experimental accuracy, 10–25%) and all the principle conclusions remain unchanged. It is mainly related to the fact that when the L concentrations in  $\text{CCl}_4$  is low, the induced shifts of the outer-sphere ligands strongly exceed the induced shifts  $\Delta\delta(E, E')$ . The choice of a standard becomes crucial at higher L concentrations when the outer-

sphere complexation effects and the shifts between standards become comparable.

The assumption of a specific interaction between the standard compounds and M is necessary to account for the effects observed. As it was shown, L ligands with high solvating ability are situated near the pyrazole rings of the complex periphery. In this case special "cavities" may appear in the region of the equatorial plane and their dimensions will depend on L. The general principle is probably as follows: the fewer L molecules there are and the stronger adducts they form, the larger are the cavities. One may assume that E molecules, interacting with M, are located in these cavities. The pseudo-contact shift for these molecules would be directed towards high fields. Taking into account the upfield shift of cyclohexane (relative to other standards) one can conclude that cyclohexane molecules penetrate into these "cavities" more easily than those of TMS and HMDS.

It should be stressed once more that we mean only specific interaction of cyclohexane with  $\text{Co}(\text{HBpz}_3)_2$ . Theoretically, pseudo-contact shift of cyclohexane might be only due to the formation of nonspecific collision complexes with M, because relatively small dimensions of cyclohexane allow it to come into closer contact with M in equatorial plane as compared with TMS and HMDS. However, in this case still larger high field shifts should be observed for such small molecules as  $\text{CH}_3\text{CN}$ . But according to Fig. 4, at higher acetonitrile concentrations when the outer-sphere complex formation effects are decreased (see (2)) cyclohexane induced shift exceed the  $\text{CH}_3\text{CN}$  one. Similar effects were found for other L solvents. Thus, it is possible to assume that the effects of collision complex formation are small and the cyclohexane life-time in the M "cavities" is larger than the life-time of collision complexes.

The nature of E–M adducts is yet unclear and further investigations are aimed at this point. Probably, the E compounds interact either with the coordinating nitrogen atoms of pyrazole rings or directly with electron orbitals of the metal ion. The latter version is more attractive since the adducts formed in this case might be treated as a model of intermediates generating under catalytic activation of alkanes. Whatever the type of E–M interactions is realized, one can draw a conclusion important for the theory of homogeneous catalysis: alkanes or any

other "inert" compounds can directly interact with the metal ions of complexes or with their nearest coordination surroundings even in solvents with the strongest solvating abilities, i.e. the metal complex solvate shell is not impenetrable. We have shown

this only for  $\text{Co}(\text{HBpz}_3)_2$ , but we think that it is also correct for a number of other complexes. The uniqueness of  $\text{Co}(\text{HBpz}_3)_2$  is that its magnetic properties facilitate direct detection of this effect.

- [1] V. M. Nekipelov and K. I. Zamaraev, *Coord. Chem. Rev.* **61**, 185 (1985).
- [2] D. R. Eaton, *Canad. J. Chem.* **47**, 2645 (1969).
- [3] D. R. Eaton, H. O. Ohorodnyk, and L. Seville, *Canad. J. Chem.* **49**, 1218 (1971).
- [4] D. R. Eaton and K. L. Chua, *Canad. J. Chem.* **51**, 4137 (1973).
- [5] J. P. Jesson, *J. Chem. Phys.* **45**, 1049 (1966).
- [6] J. P. Jesson, *NMR of Paramagnetic Molecules* (G. N. LaMar, W. DeW. Horrocks, Jr., and R. H. Holm, eds.), p. 1, Academic Press, New York 1973.
- [7] S. Trofimenko, *J. Amer. Chem. Soc.* **88**, 1842 (1966).
- [8] W. D. Horrocks, Jr., *NMR of Paramagnetic Molecules* (G. N. LaMar, W. DeW. Horrocks, Jr., and R. H. Holm, eds.), p. 127, Academic Press, New York 1973.
- [9] A. N. Kitaigorodskii, V. M. Nekipelov, and K. I. Zamaraev, *Zh. Struct. Khim.* **19**, 796 (1978).
- [10] A. N. Kitaigorodskii, V. M. Nekipelov, and K. I. Zamaraev, *Koord. Khim.* **6**, 1170 (1980).
- [11] A. N. Kitaigorodskii, *Zh. Phys. Khim.* **55**, 2025 (1981).
- [12] U. Edlund and H. Grahns, *Org. Magn. Reson.* **18**, 207 (1982).
- [13] J. P. Jesson, *J. Chem. Phys.* **47**, 582 (1967).
- [14] M. R. Churchill, K. Gold, C. E. Maw, Jr., *Inorg. Chem.* **9**, 1597 (1970).
- [15] J. Sunner and P. Kebarle, *J. Amer. Chem. Soc.* **106**, 6135 (1984).
- [16] A. N. Kitaigorodskii, *Izv. Akad. Nauk. SSSR, ser. khim.* **1985**, 1518.
- [17] N. A. Sysoeva, A. Yu. Karmilov, and A. L. Buchachenko, *Chem. Phys.* **15**, 313 (1976).