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OUTER-SPHERE COORDINATION OF ORGANIC MOLECULES TO ELECTRICALLY NEUTRAL METAL COMPLEXES

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CONTENTS

A. INTRODUCTION

The traditional description of the physico-chemical properties of metal complexes in solutions is based on a model which takes into account interactions of two types: (i) specific chemical interaction between the metal atom (ion) and the ligands of the first (inner) coordination sphere, and (ii) non-specific interaction of the inner-sphere metal complex with the medium as a dielectric continuum. The relative role of these two interactions differs substantially for electrically charged and electrically neutral metal complexes. In the former case the energy of interaction of the metal complex

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with the medium is of the same order of magnitude as that of the chemical interactions in the inner sphere, whereas in the latter case the interaction with the medium is much weaker.

In 1912 Werner indicated the possibility of an alternative approach to the description of the interaction of the inner-sphere metal complex with the medium based on the idea of the outer-sphere coordination of solvent molecules to this metal complex [1,2]. Later such terms as coordination to the second sphere, supercoordination and specific solvation were used to denote this type of coordination.

Recently the ideas of outer-sphere coordination are more and more frequently used for the description of chemical reactions of metal complexes. For example, the outer-sphere coordination of the entering ligand is often proposed to be an intermediate step for inner-sphere ligand substitution reactions [3–8].

Some direct evidence proving the existence of outer-sphere complexes (OSC) has also been obtained. For example, the outer-sphere coordination of ions and molecules having large dipole moments to *electrically charged* metal complexes has been studied in detail (see reviews [9,10] and refs. therein). The main reason for the formation of OSCs of this type seems to be the electrostatic interaction between the charged metal complex and the outer-sphere ligands [10]. There are, however, some data indicating that some more specific interactions of the donor–acceptor type can also contribute to the formation of OSCs by charged metal complexes [9].

Much less experimental data have been available for outer-sphere coordination of the solvent species to electrically neutral metal complexes.

In 1964 Clarke, Steinbach and Wagner found that the vapour pressure of liquid halomethanes depends on the concentration of transition metal acetylacetonates dissolved therein and explained this dependence by the formation of hydrogen bonds between the solvent molecules and inner-sphere ligands, namely acetylacetonate-ions [12].

A year later Frankel et al. [13] showed that chemical shifts of ^{59}Co nuclei in NMR spectra of Co(III) tris-acetylacetonate solutions are changed upon addition of chloroform in such a way that these changes can be attributed to the formation of a complex between $CHCl_3$ and $Co(acac)_3$. This effect was also accounted for by the formation of hydrogen bonds between $CHCl_3$ molecules and inner-sphere ligands.

At the same time Fackler, Davis and Chawla observed changes in the optical spectra in the visible and near-IR regions of transition metal β-diketonates upon variation of the nature of the solvent (deuterochloroform, alcohol and water) [14]. It was concluded from the analysis of IR spectra of methanol and chloroform that these solvents can form hydrogen bonds with β-diketonates [15,16].

The work [12–16] that demonstrated the possibility of formation of hydrogen bonds between metal chelates and solvent molecules made a significant contribution to the recognition of the role of outer-sphere coordination in solvation of electrically neutral complexes. Still it remained unclear whether the capability to form OSCs with organic molecules is a common feature of neutral metal complexes, whether the molecules which are not capable of forming hydrogen bonds, can enter the outer sphere, whether the outer-sphere associates have a specific structure, that is whether there is a certain energetically favorable orientation of solvent molecules near the metal complex or whether the observed effects result from random contacts during the Brownian motion, what are the coordination numbers of OSCs, etc. Therefore, the concept of existence of outer-sphere complexes as a specific type of chemical compound was not adopted until the specific orientation of the outer-sphere ligands in OSCs had been demonstrated by numerous examples, and the coordination numbers, thermodynamic characteristics and life times of OSCs in solutions had been measured.

The important advances in this field have been achieved mainly by means of NMR technique, primarily by NMR of paramagnetic particles. The variations in chemical shifts and/or relaxation rates of organic molecule nuclei upon their outer-sphere coordination to metal complexes are large enough to be detected and to provide quantitative information about the composition, structure, thermodynamic and kinetic properties of OSCs.

In 1969 Frankel [17] showed that the NMR line of the hydroxyl proton of CH_3OH was broadened much more than that of the methyl group protons upon dissolution of $Cr(acac)_3$ in methanol. A conclusion was made about the specific orientation of the CH_3OH molecules close to $Cr(acac_3)$ namely that an H atom of the hydroxyl group is less remote from the paramagnetic atom of the metal than the H atoms of the methyl group.

A year later Frankel, Stengl and Langford [18] found, also by NMR, a preferential solvation of the paramagnetic complex $Cr(acac)_3$ and of the diamagnetic complex $Co(acac)_3$ by one of the components of binary mixtures of some organic liquids. To study preferential solvation of these complexes by a substance, e.g. chloroform, two procedures were used. One of them was based on measuring the variation of the chemical shift of the ^{59}Co nucleus of $Co(acac)_3$ as a function of $CHCl_3$ concentration in the solvent, while the other was the measurement of the variation of the line-width of the $CHCl_3$ proton in the presence of $Cr(acac)_3$ as a function of $CHCl_3$ concentration. The results obtained for $CHCl_3 + CCl_4$ mixtures are illustrated in Fig. 1. Without preferential solvation of the complexes by $CHCl_3$ molecules the plots "a" and "b" in Fig. 1 would have been straight lines. The observed deviations from linearity indicate the existence of preferential solvation of metal complexes by one of the solvent components

($CHCl_3$) via formation of hydrogen bonds.

Another explanation for this phenomenon has been suggested by Eaton and coworkers [19–21]. They used NMR to study the solvation by pyridine, substituted anilines, methanol, acetonitrile, acetone, benzene, and other solvents of Co(II) trispyrazolyl-borate ($Co(HB(pz)_3)_2$)—a paramagnetic complex which has no vacancies in the inner coordination-sphere (see Fig. 2). The magnetic anisotropy of this complex is very high [22,23] which made it possible to observe significant changes of chemical shifts for solvent molecules resulting from their contacts with $Co(HB(pz)_3)_2$.

The orientation of these molecules close to $Co(HB(pz)_3)_2$ was found to occur in accordance with the direction of their dipole moments, and the

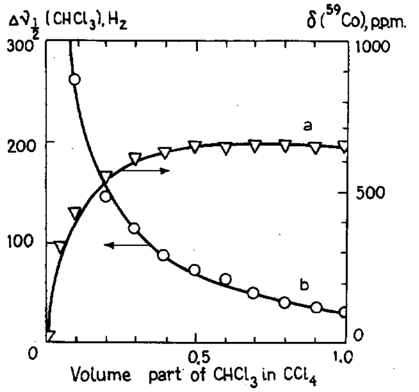

Fig. 1. Variation of the chemical shift of ^{59}Co nucleus in $Co(acac)_3$ complex (a) and of the linewidth $\Delta\nu_{1/2}$ of the proton of $CHCl_3$ in the presence of $Cr(acac)_3$ (b) in $CHCl_3 + CCl_4$ mixtures (298 K) [18].

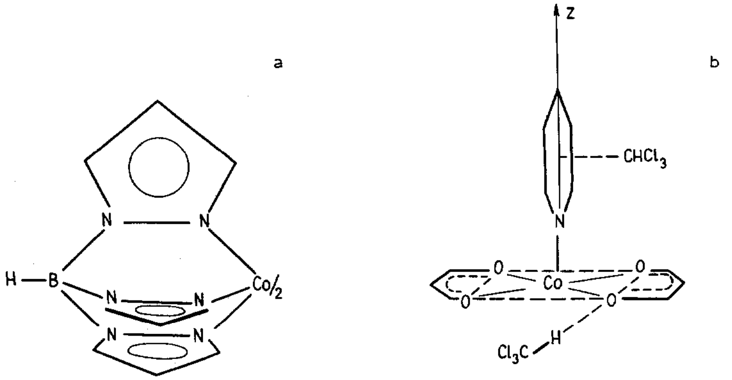

Fig. 2. Structures of Co(II) trispyrazolylborate (a) and of $Co(acac)_2py_2$ (the second molecule of pyridine is not shown in the figure) in outer-sphere complexes of various types with $CHCl_3$ (b).

stability of the associates formed to correlate with the value of the dipole moment. Thus, a conclusion was drawn that interactions responsible for the outer-sphere coordination are mainly of the electrostatic nature including those for the molecules, which are, in principle, capable of forming hydrogen bonds with $Co(HB(pz)_3)_2$. Later Chan and Eaton [24] on the basis of the measurements of nuclear spin relaxation rates of the solvent molecules concluded that $Cr(acac)_3$, for which coordination with both CH_3OH and $CHCl_3$ had previously been detected by NMR, [17,18], formed an OSC only with MeOH but not with $CHCl_3$.

The reasons for the disagreement between various authors concerning the possibility of the outer-sphere coordination of $CHCl_3$ and some other substances to transition metal complexes, as well as concerning the nature of the interaction responsible for formation of OSCs were analyzed in refs. 25, 26. The results are discussed in detail below.

Despite some contradictions in their conclusions, the NMR studies mentioned above [17–24] for the solvation of electrically neutral metal complexes by organic molecules have played an important role in showing that outer-sphere complexes indeed do exist as a specific type of compound. The authors proved reliably the existence of the preferential solvation of metal complexes by one of the components of binary mixtures. Moreover, they revealed the existence of certain favorable solvent molecule orientations close to metal complexes.

The following important step in the elucidation of the mechanism of outer-sphere solvation was made in the NMR studies of the solutions of adducts of transition metal bis-chelates of the type $M(acac)_2B$ and $M(acac)_2B_2$ where M is a transition metal, acac is the acetylacetonate ion, B is a Lewis base [27–30]. The peculiarity of these complexes in comparison with the octahedral complexes studied before is the lower (axial) symmetry of the ligand field. This peculiarity allows one to elucidate more precisely the localization of the outer-sphere ligand in the coordination sphere using NMR studies of the paramagnetic species [31]. It is known that when the ligand atom is located inside the cone with an angle $\theta = 54°$ with respect to the complex axis Z, (see the axis in Fig. 2), the dipole–dipole interaction of this atom nucleus with a paramagnetic metal induces the shift of the NMR signal to higher field relative to the signal of the same atom in a free ligand molecule in solution, whereas when the ligand atom is located outside this cone the signal is shifted to lower field [31].

It was found that adducts of Co(II) bis-acetylacetonate, such as $Co(acac)_2py_2$, where py is pyridine, interact with $CHCl_3$ and CH_2Cl_2 molecules producing OSCs of two types (see Fig. 2): via formation of hydrogen bonds with oxygen atoms of the equatorial inner-sphere chelate ligands (more stable OSCs) and via interaction with the π-system of the axial inner-sphere ligands (less stable OSCs) [32]. Thus, it was proven that a metal complex is capable of forming several types of OSCs in which the same outer-sphere ligands are localized at different sites.

The next important step in the development of the idea that OSCs are a specific type of compound with a certain composition was the measurement of the coordination numbers of various metal complexes with respect to outer-sphere ligands [26–33]. Such measurements were made for OSCs of Cu(II), Fe(III) and Cr(III) acetylacetonates with chloroform, dichloromethane, dichloroethane, acetone, benzene and other organic substances using a procedure based on the comparison of the solubility of these chelate complexes and the relaxation rates of the outer-sphere ligand nuclei in the same binary mixtures of organic liquids. The outer-sphere complex formation was found to be of a discrete (stepwise) character, the maximum coordination number of OSCs being equal to the number of the inner-sphere chelate ligands. This result directly indicates that, at least in the case of metal acetylacetonates, the formation of OSCs with various organic compounds results from specific (although rather weak) interactions between outer- and inner-sphere ligands.

An interesting result was the detection of low, although still noticeable, delocalization of spin density ($\rho \sim 10^{-5}$) onto the protons of such molecules as $CHCl_3$, CH_2Cl_2 and MeOH upon their outer-sphere coordination to the charged ($[MI_3PPh_3]^-$ $[NBu_4]^+$, where M = Co(II) or Ni(II), [34] and to the electrically neutral $Cr(acac)_3$, [24,35]) transition metal complexes. Later it was found that the spin density transfer from the metal atom occurs not only onto the protons but also onto other nuclei of the outer-sphere ligands. This phenomenon was observed for such outer-sphere ligands as alkyl halides [36–43], acetone and acetonitrile [41], aromatic molecules [44], hydroperoxide of isopropylbenzene [45,46] and alcohols [47]. The transfer of the spin density onto the outer-sphere ligands clearly indicates that the interactions responsible for the formation of OSCs between the substances mentioned above and $Cr(acac)_3$ are not purely electrostatic.

A systematic study of the interactions leading to the formation of OSCs was carried out by Kitaigorodskii, Nekipelov and Zamaraev in 1978 [25] using tris-β-diketonates of various transition metals. It was found that the molecules which are proton donors, even if very weak ones (acids, alcohols, alkyl halides etc.), can form OSCs via hydrogen bonds with the oxygen atoms of the inner-sphere ligands, whereas the molecules having no proton-donating properties (acetone, acetonitrile, benzene, toluene) seem to form OSCs via the interaction of their π-systems with the π-system of the inner-sphere chelate ligands. Formation of OSCs via the interaction of the π-systems of the outer-sphere and the inner-sphere ligands was also clearly demonstrated in 1976 by Fulton and La Mar [48,49] for the OSC between

1,3,5-trinitrobenzene and tetra-*p*-tolylporphin Co(II).

Thus, both in metal complexes and in outer-sphere ligands it is possible to distinguish certain functional groups responsible for outer-sphere coordination. Thus outer-sphere associates formed by electrically neutral metal complexes can be regarded as unstable but still specific chemical compounds.

Many attempts have been made to estimate the stability constant and heat effect of the formation of OSCs [18–21,27,28,35,48,49]. In most cases it was assumed that the outer-sphere complexes had the composition 1 : 1. Meanwhile, as has been mentioned above, the outer-sphere coordination is a stepwise process and the total coordination numbers for OSCs are usually other than unity. Therefore, thermodynamic characteristics obtained without taking this fact into account should be regarded with suspicion. A detailed study of the thermodynamics of OSC formation taking into account a stepwise method of outer-sphere coordination and possible formation of complexes with high coordination numbers was carried out by Kitaigorodskii et al. in 1978 [25]. The thermodynamic results of outer-sphere coordination will be discussed in more detail in section B. However, note that several examples are known [50] when outer-sphere complexes of some Lewis bases with square-planar transition metal chelates have even higher stability constants than the inner-sphere adducts of these bases with the same chelates.

An important step was also the measurement of the rates of OSC formation and decomposition using NMR [51]. Such measurements were made for complexes of $Cr(acac)_3$ and $Fe(acac)_3$ with $CHCl_3$, CH_2Cl_2, MeOH and acetone. At room temperature the typical life time of the OSCs was found to be 10^{-10} s and the activation energy of their decomposition was found to be close to the heat of their dissociation. Thus, OSCs are very labile compounds.

For a long time, investigation of outer-sphere coordination was performed using predominantly proton magnetic resonance (PMR) of paramagnetic metal complexes since variation of chemical shifts and rates of nuclear relaxation of hydrogen atoms of ligands in the outer coordination sphere of such complexes are large enough to be reliably measured. For diamagnetic complexes for which these variations are far less marked a study of OSCs using PMR spectra of outer-sphere ligands was less fruitful. However, it has been found recently that outer-sphere coordination of organic ligands with diamagnetic complexes can be detected reliably and studied provided that deuterated substances are used as such ligands [52]. The deuterium nucleus has a quadrupole moment, distinct from the proton. The rate of the quadrupole relaxation of deuterium nuclei in organic molecules changes upon outer-sphere coordination to such an extent that this change can be reliably measured. For example, the stability constants and lifetimes of the outer-sphere complex between $CDCl_3$ and $Co(acac)_3$ have been measured using the quadrupole relaxation method [52].

Outer-sphere coordination of solvent molecules to metal complexes has also recently been studied using X-ray analysis. For example, X-ray studies of $Pd(acac)(CH_2COOH)PPh_3$ [53] have indicated that a molecule of acetic acid is stabilized in the outer-sphere of this complex owing to formation of a hydrogen bond (Fig. 3). X-ray data also show that in the OSC of $Co(acac)_3$ with β-naphthol [54] the latter is bound to $Co(acac)_3$ via a hydrogen bond formed between the OH-group of β-naphthol and the oxygen atom of the inner-sphere ligand (see Fig. 3). Simultaneous with the study of OCS formation, the influence of outer-sphere coordination of the solvent molecules on the structure and properties of metal complexes in solutions has also been studied. The addition of outer-sphere ligands can notably perturb the electronic structure of metal complexes. Such perturbations were elucidated by observing large changes in the chemical shifts of metal atoms [18] and of atoms of inner-sphere ligands in diamagnetic metal complexes [55] as well as in changes of magnetic anisotropy in paramagnetic metal complexes [48,49,56] and of their zero-field splitting [57,58]. Moreover, it is possible to observe the change in spin state of certain metal complexes under the influence of outer-sphere interaction [59–61].

Outer-sphere coordination was also found to affect the geometric structure of the inner coordination sphere of metal complexes. Significant changes in the length of chemical bonds between the metal atom and coordinating atoms of the inner-sphere ligands [30] as well as a change from square-planar to tetrahedral structure upon variation of the composition of the outer coordination sphere [62] have been detected.

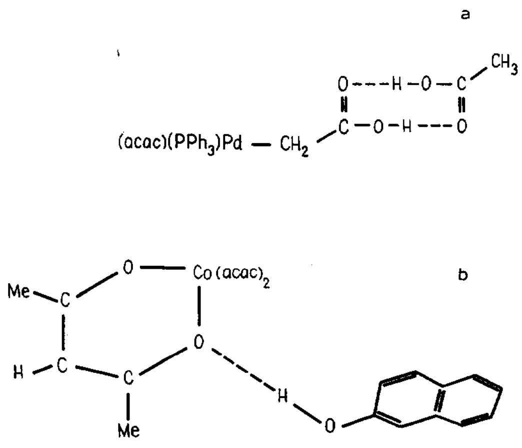

Fig. 3. Structure of the outer-sphere complex of $Pd(acac)(CH_2COOH)PPh_3$ with CH_3COOH [53] (a) and of $Co(acac)_3$ with β-naphthol [54] (b).

Outer-sphere coordination can also considerably affect the physico-chemical properties of metal complexes in solutions. For example, the solubility of metal complexes can be changed significantly upon the influence of outer-sphere coordination [63]. Outer-sphere coordination was reported also to influence the reactivity of metal complexes. For example, Boate and Eaton in 1976 [64–66] used NMR to study the mechanism of formation and hydrolysis of substituted anils in non-aqueous media in the presence of Co(II), Ni(II) and Zn(II) complexes with thiourea as catalysts. The rate determining step for the reaction of formation of anils seems to be nucleophilic attack on the molecule of acetone located in the inner coordination sphere by molecules of aniline located in the outer coordination sphere.

Another example seems to be the catalytic reaction of the formation of urethanes in the presence of $Fe(acac)_3$ [67]. According to data obtained by kinetic and NMR studies the most likely process occurs via preliminary coordination of one reagent in the inner-sphere of the catalyst and of another reagent in the outer-sphere, followed by the formation of the active intermediate (the complex of the alcohol with the isocyanide) which has a structure similar to that of the final product (urethane).

Thus, outer-sphere coordination of organic molecules to electrically neutral transition metal compounds seems to be a reliably established fact. In this review the studies of the structure and properties of OSCs and their action on reactivity of metal complexes will be discussed.

B. THERMODYNAMICS OF THE OUTER-SPHERE COORDINATION

(i) Peculiarities of measurements of stability constants for outer-sphere complexes

We have already mentioned that changes in the spectra of both the initial metal complex M and of outer-sphere ligands L can be observed when OSCs are formed. Depending on the spectroscopic method employed, there occurs either fast or slow exchange of ligands on the time scale of the method. For example, in the IR spectra the lines corresponding to the vibrations of the hydroxyl protons of methanol in the free and coordinated states can be observed separately [15,16]. In this case, estimation of the thermodynamic parameters of OSCs is not difficult because the ratios between the concentrations of the free and coordinated methanol can be readily calculated from the ratios of intensities of these lines.

Most of the information concerning the thermodynamic properties of OSCs has been obtained using NMR. NMR studies are usually carried out in the conditions of a fast exchange of L between OSC and a free state in solution. The values of the spectroscopic parameters observed for L and M are actually the averages for the free and coordinated states of these species. For the stepwise mechanism of the formation of an OSC with coordination number N

$$M + NL \overset{K_1}{\rightleftharpoons} ML + (N-1)L \overset{K_2}{\rightleftharpoons} \ldots \overset{K_{N-1}}{\rightleftharpoons} ML_{N-1} + L \rightleftharpoons ML_N \tag{1}$$

which occurs under fast exchange conditions, the observed change of a parameter κ of the NMR spectrum of metal complex M or ligand L upon formation of OSCs can be represented as

$$\Delta\kappa = \sum_{i=1}^{N} p_i \Delta\kappa_i \tag{2}$$

where $\Delta\kappa_i$ is the difference between the values of parameter κ for the OSC ML_i and for substances M or L in the free states; $p_i = [ML_i]/[M]_0$ if the change in the spectrum of M is analyzed, and $p_i = i[ML_i]/[L]_0$ if the spectrum of L is analyzed. Chemical shifts δ, rates of spin–lattice (R_1) and spin–spin (R_2) nuclear relaxation as well as the width of NMR lines (which is related to R_2 through the relation $R_2 = \pi\Delta\nu_{1/2}$) for various nuclei of M and L can play the role of parameter κ.

Experimental conditions are usually selected so that for the total concentrations of M and L the ratio $[M]_0 \ll [L]_0$ is fulfilled. Then,taking into account the equation of the material balance

$$[M]_0 = [M] + \sum_{i=1}^{N} [ML_i] \tag{3}$$

and $[L]_0 = [L]$, one has for equilibrium (1)

$$[ML_i] = [M]_0 \frac{[L]_0^i \prod_{j=1}^{i} K_j}{1 + \sum_{i=1}^{N} [L]_0^i \prod_{j=1}^{i} K_j} \tag{4a}$$

where

$$K_j = [ML_j]/([ML_{j-1}][L]) \tag{4b}$$

By substituting expressions (4a) and (4b) into (2) one arrives at

$$\Delta\kappa = \frac{\sum_{i=1}^{N} \alpha_i \Delta\kappa_i [L]_0^i \prod_{j=1}^{i} K_j}{1 + \sum_{i=1}^{N} [L]_0^i \prod_{j=1}^{i} K_j} \tag{5}$$

It can be readily seen that this dependence corresponds qualitatively to the plot (a) in Fig. 1 for $\alpha_i = 1$ (spectra of M) and to the plot (b) in Fig. 1 for $\alpha_i = i[\mathrm{M}]_0/[\mathrm{L}]_0$ (spectra of L). At the same time it is clear that in its general form, expression (5) is rather complicated. However, when applied to the study of OSC formation, the dependence (5) can be considerably simplified [68] because the conditions of the thermodynamic and structural equivalency are often fulfilled for similar sites of outer-sphere coordination. These conditions are expected to be fulfilled, e.g., for the OSCs of tris–β–diketonate complexes having three equivalent inner-sphere ligands. In section B.(ii) we shall present some evidence for the validity of this idea.

In the case of the thermodynamic equivalency of various coordination sites, the constants K_j will differ from each other only in the values of the statistical factor [69]. This means that the probability of dissociation of OSC ML_j will be proportional to the number, j, of its outer-sphere ligands, whereas the probability of its formation will be proportional to the number of vacancies in the coordination sphere of its precursor, namely the OSC ML_{j-1}. With these conditions the following relationship is valid [69]:

$$K_j = \beta(N - j + 1)/j \tag{6}$$

where β is the temperature-dependent parameter which is the same for all K_j.

Taking (6) into account one can transform, according to [68], the denominator in formula (5) to a quite compact expression

$$Z = 1 + \sum_{i=1}^{N} [\mathrm{L}]_0^i \beta^i \frac{N!}{i!(N-i)!} = (1 + \beta[L]_0)^N \tag{7}$$

In the case of the structural equivalency of various sites of the outer-sphere coordination the values of $\Delta\kappa$ will be the same for all coordinated molecules of L in all complexes ML_i, i.e. the condition $\Delta\kappa_i = \Delta\kappa^{(\mathrm{M})}$ will be fulfilled for all values of i. In this situation the value of $\Delta\kappa$ for a spectroscopic parameter can be given as

$$\Delta\kappa = \Delta\kappa^{(\mathrm{M})}[\mathrm{M}]_0 Z^{-1} \sum_{i=1}^{N} i[\mathrm{L}]_0^{i-1} \prod_{j-1}^{i} K_j \tag{8}$$

It is seen that the right-hand part of eqn. (8) is equal to the derivative of the value Z (see expression (7)) with respect to the total concentration of ligand L. Therefore,

$$\begin{aligned}\Delta\kappa &= \Delta\kappa^{(\mathrm{M})}[\mathrm{M}]_0 Z^{-1} \mathrm{d}Z/\mathrm{d}[\mathrm{L}]_0 = \Delta\kappa^{(\mathrm{M})}[\mathrm{M}]_0 \mathrm{d}(\ln Z)/\mathrm{d}[\mathrm{L}]_0 \\ &= \Delta\kappa^{(\mathrm{M})} N[\mathrm{M}]_0 \beta(1 + \beta[\mathrm{L}]_0)^{-1}\end{aligned} \tag{9}$$

A similar formula can also be derived for the variations in spectroscopic parameters $\Delta\kappa$ of complex M if one assumes that the variations of these parameters upon addition of every new molecule of the outer-sphere ligand are independent of the number of such ligands already present in the coordination sphere of M, i.e. one deals with additive variations in $\Delta\kappa$: $\Delta\kappa_i = i\Delta\kappa^{(M)}$.

In this case

$$\Delta\kappa = \Delta\kappa^{(M)} N [L]_0 \beta (1 + \beta [L]_0)^{-1} \tag{10}$$

It follows from equations (9) and (10) that in the case of structural and thermodynamic equivalency of the sites of the outer-sphere coordination, variations in spectroscopic parameters of both M and L are described by the law typical for the one-step mechanism of the formation of OSCs with the stability constant equal to β and the concentration of the initial complex equal to $N[M]_0$. This fact has clear physical meaning. In fact, since all the coordination sites are equivalent, one can use the same value of the stability constant for all the sites and the value of $N[M]_0$ for concentration of the sites to derive thermodynamic relations. The fact that some of the equivalent sites are located on the same metal complex is of no significance.

Thus, outer-sphere coordination can be regarded from the thermodynamic standpoint as addition of L to isolated sites of the outer-sphere coordination, C, whose concentration is $[C]_0 = N[M]_0$.

The above formulae correspond to an ideal system in which no self-association of L occurs, and the solvent S does not compete with L for the formation of OSCs and does not produce associates with L in solution. In reality the situation, of course, is much more complicated.

Consider, first, the situation where two outer-sphere ligands L and S compete for equivalent sites of the coordination of compound C:

$$\begin{gathered} C + L \overset{\beta}{\rightleftharpoons} CL \\ C + S \overset{\beta_s}{\rightleftharpoons} CS \end{gathered} \tag{11}$$

the condition being fulfilled $[C]_0 = N[M]_0 \ll [L]_0, [S]_0$.

Taking into account the equations of the material balance one has

$$[CL] = [C]_0 \beta [L]_0 (1 + \beta [L]_0 + \beta_s [S]_0)^{-1}$$

From variation in spectroscopic parameters of L, one obtains

$$\Delta\kappa = \Delta\kappa^{(M)} N [M]_0 \beta (1 + \beta [L]_0 + \beta_s [S]_0)^{-1} \tag{12}$$

We now discuss the practically important situation of a binary L + S mixture in which the concentrations of the components are varied by way of mutual dilution. When the total volume of liquids remains unchanged upon mixing, the following relationship is valid:

$$[\mathrm{L}]_0/[\mathrm{L}]^* + [\mathrm{S}]_0/[\mathrm{S}]^* = 1 \tag{13}$$

where [L]* and [S]* are the concentrations of pure substances L and S. Using expressions (12) and (13) one obtains

$$\Delta\kappa = \Delta\kappa^{(\mathrm{M})} N [\mathrm{M}]_0 \beta [1 + \beta_s [\mathrm{S}]^* + [\mathrm{L}]_0 (\beta - \beta_s [\mathrm{S}]^*/[\mathrm{L}]^*)]^{-1} \tag{14}$$

It is seen that when the condition $\beta_s[\mathrm{S}]^* = \beta[\mathrm{L}]^*$ is fulfilled the value of $\Delta\kappa$ will be independent of the composition of the mixture. It will be shown below that just this relationship is valid for the $CH_2Cl_2 + CHCl_3$ mixture. This is the reason for the absence of variation in the rate of paramagnetic relaxation of protons of these complexes in the presence of $Cr(acac)_3$ upon variation of the relative concentration of the components [24], despite the fact that both CH_2Cl_2 and $CHCl_3$ are capable of forming OSCs with $Cr(acac)_3$. It can also be shown that for $\beta_s[\mathrm{S}]^* \neq \beta[\mathrm{L}]^*$, expression (14) which describes the dependence of $\Delta\kappa$ on $[\mathrm{L}]_0$ can be presented in the same form as eqn. (9):

$$\Delta\kappa = \Delta\kappa_{\mathrm{eff}}^{(\mathrm{M})} N [\mathrm{M}]_0 \beta_{\mathrm{eff}} (1 + \beta_{\mathrm{eff}} [\mathrm{L}]_0)^{-1}$$

with an effective stability constant

$$\beta_{\mathrm{eff}} = (\beta - \beta_s [\mathrm{S}]^*/[\mathrm{L}]^*)(1 + \beta_s [\mathrm{S}]^*)^{-1} \tag{15}$$

and an effective change in the parameter κ.

$$\Delta\kappa_{\mathrm{eff}}^{(\mathrm{M})} = \Delta\kappa^{(\mathrm{M})} \beta (\beta - \beta_s [\mathrm{S}]^*/[\mathrm{L}]^*)^{-1}$$

Note that from the sign of β_{eff} one can determine immediately which of the solvents, L or S, is more effective in forming OSCs with M.

Thus, for equivalent coordination sites, variation in spectroscopic parameters of L in binary L + S mixtures in which S competes with L are also described by a simple law typical for the one-step mechanism of the formation of OSCs. However, the effective stability constant β_{eff} and effective change in the spectroscopic parameter $\Delta\kappa_{\mathrm{eff}}^{(\mathrm{M})}$, of course, differ in their physical meaning from the parameters for the simplest scheme of addition to M of one molecule of L.

Let us now analyze another situation which is also important for our further discussion, namely the situation where ligand L coordinates with M to produce two different types of OSCs. The coordination process in this case is described as

$$
\begin{aligned}
&C + L \overset{\beta_{CL}}{\rightleftharpoons} CL \\
&C + S \overset{\beta_{CS}}{\rightleftharpoons} CS \\
&B + L \overset{\beta_{BL}}{\rightleftharpoons} BL \\
&B + S \overset{\beta_{BS}}{\rightleftharpoons} BS
\end{aligned}
\tag{16}
$$

where B defines the coordination sites of the second type. If the coordination of L with C and B occurs independently and if one takes into account the material balance conditions

$$
\begin{aligned}
&[C]_0 = [C] + [CL] + [CS] \\
&[B]_0 = [B] + [BL] + [BS]
\end{aligned}
\tag{17}
$$

one obtains

$$
\begin{aligned}
&[CL] = \beta_C[C]_0[L]_0(1 + \beta_C[L]_0)^{-1} \\
&[BL] = \beta_B[B]_0[L]_0(1 + \beta_B[L]_0)^{-1}
\end{aligned}
\tag{18}
$$

where

$$
\begin{aligned}
&\beta_C = (\beta_{CL} - \beta_{CS}[S]^*/[L]^*)(1 + \beta_{CS}[S]^*)^{-1} \\
&\beta_B = (\beta_{BL} - \beta_{BS}[S]^*/[L]^*)(1 + \beta_{BS}[S]^*)^{-1}
\end{aligned}
\tag{19}
$$

It is seen that the concentrations [CL] and [BL] are changed independently upon variation of $[L]_0$ and, consequently, they can be described by individual stability constants, β_C and β_B.

Still another situation is possible where the formation of complex CL precludes the possibility of formation of complex BL, and vice versa. In this case the condition for material balance has to be written as

$$
\begin{aligned}
&[C]_0 = [C] + [CL] + [CS] + [BL] \\
&[B]_0 = [B] + [BL] + [BS] + [CL]
\end{aligned}
\tag{20}
$$

Taking (20) into account one obtains

$$
[CL] = \frac{\beta_C[C]_0[L]_0 + ([C]_0 - [B]_0)\beta_C\beta_B[L]_0^2}{1 + (\beta_B + \beta_C)[L]_0}
\tag{21a}
$$

$$[\mathrm{BL}] = \frac{\beta_{\mathrm{B}}[\mathrm{B}]_0[\mathrm{L}]_0 + ([\mathrm{B}]_0 - [\mathrm{C}]_0)\beta_{\mathrm{C}}\beta_{\mathrm{B}}[\mathrm{L}]_0^2}{1 + (\beta_{\mathrm{B}} + \beta_{\mathrm{C}})[\mathrm{L}]_0} \tag{21b}$$

where β_C and β_B are given by formula (19).

When $[B]_0 = [C]_0$, that is, when the coordination numbers N are the same for the two types of coordination, it can easily be proven that variations in the concentrations [CL] and [BL] upon variation of $[L]_0$ are described by the common stability constant $\beta = \beta_C + \beta_B$, the ratio of their concentrations being equal to $[CL]/[BL] = \beta_C/\beta_B$.

A similar conclusion about the common stability constant for two mutually exclusive types of coordination has also been drawn by Buchachenko and co-workers who studied the processes of association of free radicals with organic molecules [70].

Association of molecules L with the solvent is generally expected to lead to a decrease of the effective stability constant of OSC. In fact, for the simplest competitive process

$$\begin{aligned} &\mathrm{C} + \mathrm{L} \rightleftharpoons \mathrm{CL} \\ &\mathrm{S} + \mathrm{L} \rightleftharpoons \mathrm{SL} \end{aligned} \tag{22}$$

for $[L]_0 \ll [S]_0$ one obtains

$$[\mathrm{L}] = [\mathrm{L}]_0(1 + K_{\mathrm{SL}}[\mathrm{S}]_0)^{-1},$$

where

$$K_{\mathrm{SL}} = [\mathrm{SL}][\mathrm{S}]^{-1}[\mathrm{L}]^{-1}$$

In this case

$$[\mathrm{CL}] = [\mathrm{C}]_0\beta_{\mathrm{eff}}[\mathrm{L}]_0(1 + \beta_{\mathrm{eff}}[\mathrm{L}]_0)^{-1}$$

where

$$\beta_{\mathrm{eff}} = \beta(1 + K_{\mathrm{SL}}[\mathrm{S}]_0)^{-1} \tag{23}$$

Thus, association of L with the solvent decreases β by a factor of $1 + K_{SL}[S]_0$. At an arbitrary $[L]_0$ to $[S]_0$ ratio the effect of the decrease of β upon addition of L has the same qualitative character. However, analysis of its absolute value is much more complicated. In particular, there can arise the situation where β_{eff} will depend on [L], i.e. some deviations from the simplest dependence of the type (9) will be observed.

Complex dependence of β on the concentration of L can also be expected if self-association of L takes place. In order to reveal the character of the influence of this self-association on the dependence between $\Delta\kappa$ and $[L]_0$, let us consider association of the solvent according to the scheme

$$nL \overset{K_n}{\rightleftharpoons} L_n$$

where $K_n = [L_n]/[L]^n$ can acquire arbitrary values. Assume that both monomers L and associates L_n take part in formation of OSCs, but the change of $\Delta\kappa$ occurs only in one molecule of the associate L_n, namely in the molecule which is directly involved in the formation of the bond with complex M. Such an assumption, indeed, seems to be justified for NMR spectroscopic parameters of organic molecules whose perturbation upon formation of adducts with paramagnetic complexes is known to decrease drastically as the distance between the molecule under study and the paramagnetic metal increases.

No special calculations are needed to show for extreme cases of low concentrations of L such that $K_n[L]_0^{n-1} \ll 1$ and $\beta[L]_0 \ll 1$ and high concentrations of L such that $K_n[L]_0^{n-1} \gg 1$, $\beta[L]_0 \gg 1$, the expressions for $\Delta\kappa$ will be the same as those resulting from eqn. (9)

$$\Delta\kappa = \Delta\kappa^{(M)} N[M]_0 \beta(1 - \beta[L]_0)$$

and

$$\Delta\kappa = \Delta\kappa^{(M)} N[M]_0 [L]_0^{-1}$$

In fact, for low $[L]_0$ only monomers L are present in the solution, the coordination of which can be described by scheme (1). For high $[L]_0$ all the sites in the outer coordination sphere of M are occupied by the molecules of L and the parameter $\Delta\kappa$ is determined only by the ratio of the number of molecules of L in the coordination sphere and in the solution.

Thus, in the extreme cases discussed, self-association of the solvent does not affect the form of the dependence of $\Delta\kappa$ on $[L]_0$. Deviations from the dependence (9) can be detected only for intermediate values of $[L]_0$ when the conditions $K_n[L]_0^{n-1} \simeq 1$ and/or $\beta[L]_0 \simeq 1$ are satisfied.

(ii) Coordination numbers of outer-sphere complexes. Effect of the outer-sphere coordination on solubility of metal complexes

Following from formulae (3) and (7), under the conditions of site equivalency of outer-sphere coordination, the total concentration, $[M]_0$, of the metal complex in solution is related to its concentration, [M], in a free state through the expression:

$$[M]_0 = [M]\left(1 + \sum_{i=1}^{N} [L]_0^i \prod_{j=1}^{i} K_j\right) = [M](1 + \beta[L]_0)^N \tag{24}$$

When these conditions are fulfilled, the formula (9) is also valid for variations $\Delta\kappa$ of the spectroscopic parameters of L. A comparison of eqns. (9) and (24) suggests that a log plot of the dependence between the total concentration of a metal complex in saturated solutions containing an inert (i.e. not capable of forming OSCs) solvent and various amounts of the outer-sphere ligands L (i.e. solubility $[M]^*$ in this solution), and the values of $\Delta\kappa^{-1}$ measured in the same L + S mixture containing fixed concentration of the metal complex $[M]_0 < [M]^*$, will be a straight line with a slope equal to N.

In fact if at all concentrations of L, the same substance, namely unsolvated complex M, is precipitated from saturated solutions, the value of its concentration [M] has to remain constant at any (although not very high, see below) concentration of L. In this case using eqns. (24) and (9) one obtains

$$\log[M]^* = N\log(\Delta\kappa^{-1}) + \text{const} \tag{25a}$$

where

$$\text{const.} = \log[M] + N\log(N[M]_0\Delta\kappa^{(M)}\beta) \tag{25b}$$

A certain correlation between the solubility $[M]^*$ of metal complexes and the variation in the relaxation rates of the protons of the solvent was found [63]. Later this effect was analyzed quantitatively, and as a result, the coordination numbers for a series of OSCs were determined [26].

In Fig. 4 the values of the solubility $[M]^*$ of the complex $Cr(acac)_3$ in the presence of a series of substances such as $CHCl_3$, CH_2Cl_2, CH_2Cl-CH_2Cl, $(CH_3)_2CO$, C_6H_6, all of which produce OSCs with this complex, are compared with the times T_1 of spin–lattice relaxation of protons of these

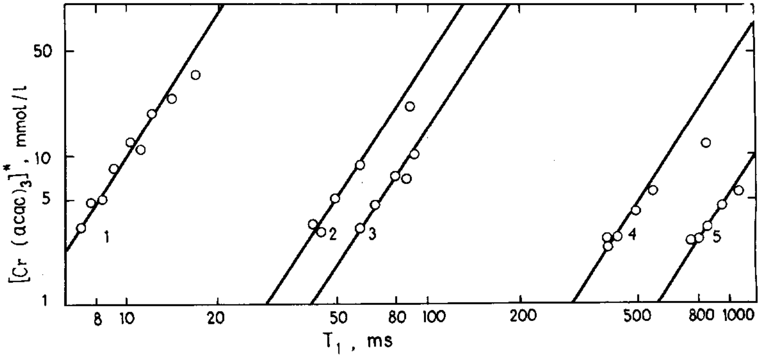

Fig. 4. Solubility of $Cr(acac)_3$ in mixtures of cyclohexane with $CHCl_3$ (1), CH_2Cl_2 (2), CH_2Cl-CH_2Cl (3), $(CH_3)_2CO$(4), and C_6H_6 (5) vs. time of spin–lattice relaxation of protons of these ligands in the same mixtures in the presence of 2.0 mmol l^{-1} $Cr(acac)_3$.

substances in the same solutions but containing $Cr(acac)_3$ with concentration 2.0×10^{-3} mol l^{-1}, which is smaller than $[M]^*$. In this case, $\Delta\kappa = R_1$ is the rate of paramagnetic spin–lattice relaxation, $\Delta\kappa^{-1} = R_1^{-1} = T_1$. Different points correspond to different concentrations of outer-sphere ligands whose variations lead to the change of both $[M]^*$ and T_1. Cyclohexane which does not produce outer-sphere complexes with transition metal β–diketonates [25,28] was used as an inert solvent, S. At sufficiently low concentrations of L ($[L]_0 < 0.5$ mol l^{-1}) the experimental dependence of log $[M]^*$ on log T_1 was found to be, indeed, close to linear for all the outer-sphere ligands studied, the experimental points being located close to solid lines corresponding to $N = 3$.

It follows from eqn. (25) that the plot of the dependence of $[M]^*$ on T_1 in logarithmic coordinates is expected to be a straight line only when the concentration of the unsolvated complex M in saturated solutions changes negligibly upon variation of the concentration of L. Let us show now that this condition is indeed satisfied for $[M]^* \ll [L]_0 \ll [S]_0$.

For a saturated solution the following relationship is valid [71]:

$$\mu_M = \psi + kT\log[M] = \mu_0 \tag{26}$$

where μ_M is the chemical potential of the unsolvated metal complex in the solution; ψ is the part of this potential which characterizes a nonspecific interaction of M with the solvent and is independent of $[M]^*$ for $[M]^* \ll [L]_0$, $[S]_0$; μ_0 is the chemical potential of the metal complex M in the solid phase (note again that the same compound, namely, unsolvated metal complex M is assumed to be precipitated from all solutions). For $[L]_0 \ll [S]_0$, i.e. when the nearest neighbours of the unsolvated metal complex M consist almost entirely of the molecules of inert solvent S, the potential ψ will be independent of $[L]_0$. In this situation, as follows from eqn. (26), [M] will also be independent on $[L]_0$. At the same time, for high values of $[L]_0$, ψ will start to change upon variation of L_0. In this case the dependences between log$[M]^*$ and $\log(\Delta\kappa)^{-1}$ will deviate from linearity, a fact actually observed in the experiments (see Fig. 4).

The coordination numbers N of OSCs for a series of complexes are compiled in Table 1. They have been obtained from the experimental plots of Fig. 4 for $Cr(acac)_3$ and similar plots for other complexes using the least-square analysis. As is seen in the Table, $Cr(acac)_3$ and $Fe(acac)_3$ interact with the ligands to produce OSCs of the composition 3 : 1, while $Cu(acac)_2$ produces OSCs of the composition 2 : 1. This is in agreement with the measurements of coordination number $N = 2.1 \pm 1.1$ for OSCs between chloroform and $Cu(acac)_2$ made by Raut and Meloan [72] using chromatographic and extraction methods. Thus for the organic molecules studied, the coordination number N of OSCs coincides with the number of acetyla-

TABLE 1

Stoichiometric composition of outer-sphere complexes in cyclohexane [26]

Metal complex	Outer-sphere ligand	N [a]
$Cr(acac)_3$	chloroform	3.0 ± 0.4
	dichloromethane	3.1 ± 0.6
	dichloroethane	2.9 ± 0.6
	acetone	2.5 ± 0.8
	benzene	2.7 ± 0.8
	trichloroethylene [43]	3.6 ± 0.3
$Fe(acac)_3$	chloroform	3.1 ± 0.5
$Cu(acac)_2$	chloroform	1.7 ± 0.7

[a] N = No. of outer-sphere ligands.

cetonate ligands in the inner coordination sphere.

It follows from eqn. (9) that the dependence of $\Delta\kappa$ on $[L]_0$ should give a straight line in the coordinates $\{\Delta\kappa^{-1}; [L]_0\}$ not only for the formation of complexes of the composition 1 : 1, but also for the formation of complexes with higher coordination numbers, provided that the sites of the outer-sphere coordination are equivalent. Such dependence for the rate $R_1 = T_1^{-1}$ of CH_2Cl_2 proton relaxation caused by the outer-sphere coordination of CH_2Cl_2 to $Cr(acac)_3$ is presented in Fig. 5. This dependence, as well as those for other outer-sphere ligands L studied by us, gives straight lines in the coordinates $\{T_1; [L]_0^{-1}\}$. This fact provides additional evidence for the validity of the assumption of the equivalency of the coordination sites of

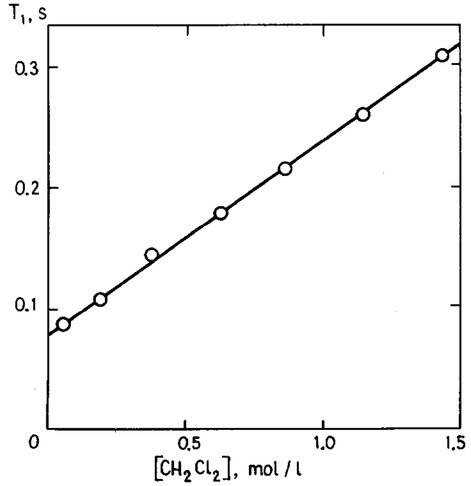

Fig. 5. Time of spin–lattice relaxation T_1 of CH_2Cl_2 protons vs. CH_2Cl_2 concentration in the solutions of C_6H_{12} containing 0.95 mmol l^{-1} $Cr(acac)_3$ (298 K) [24].

OSCs formed by the acetylacetonates of various metals.

Note that the OSC coordination numbers have been determined above from the comparison of the data obtained by measuring the two independent parameters: solubility [M]* of the metal complex and its NMR parameter $\Delta\kappa$. By measuring only $\Delta\kappa$ for various values of $[L]_0$ it is possible to calculate only β and the product $\Delta\kappa^{(M)}N$, as follows from eqns. (9) and (10). Usually the value of $\Delta\kappa^{(M)}$ is unknown and therefore, N cannot be measured reliably solely by using spectroscopic methods. For example, it seems to us that the value $N = 8$ [24] for the OSCs of $Cr(acac)_3$ with methanol obtained using NMR only is too high.

(iii) Stability constants of outer-sphere complexes

OSC stability constants were first measured by Eaton and Chua [21]. Assuming that complexes of composition 1 : 1 are formed, relative stability constants of OSCs between Co(III)–pyrazolylborate, $Co(HB(pz)_3)_2$, and various organic solvents were found. CCl_4 was used as a reference solvent. In terms of the approach described in Section B.(i), based on the assumption of energetic and structural equivalency of coordination sites, the stability constants measured in [21] and listed in Table 2 correspond to the β/β_{CCl_4} ratio. As seen in Table 2, there is a correlation, though not quite distinct, between the values of β/β_{CCl_4} and those of the dipole moment of the solvent.

Systematic studies of OSC stability constants between transition metal diketonates and various organic molecules were carried out [25–30,43]. The values of β measured, as well as those calculated from the data obtained by other authors, are listed in Tables 3, 4 and 5. Two types of procedures were used in these measurements: the study of the concentration dependence for the relaxation rates (R_1 and R_2) and of the NMR linewidth $\Delta\nu_{1/2}$ of the protons of organic molecules, and the study of the concentration dependence

TABLE 2

Relative stability constants of outer-sphere complexes of $Co(HB(pz)_3)_2$ with organic molecules and the dipole moments of these molecules [21]

Outer-sphere ligand	β/β_{CCl_4}	Dipole moment
Acetonitrile	8.2	3.92
Acetone	8.2	2.88
Methanol	4.7	1.70
Dichloromethane	2.0	1.60
Benzene	1.25	0
Cyclohexene	1.18	0
Cyclohexane	0.52	0

TABLE 3

Stability constants (298 K) of outer-sphere complexes in cyclohexane

Ligand	Metal complex	$\beta^{(H)}$(l mol^{-1}) [a]	Ref.
Chloroform	$Co(acac)_2py_2$	3.7	[32]
	$Co(acac)_2py_2$	3.0	[b]
	$Co(acac)_2(\gamma\text{-pic})_2$	3.1	[b]
	$Co(acac)_2(pipe)_2$	2.0	[29]
	$Cu(acac)_2$	2.5	[26]
	$Cr(acac)_3$	3.1	[25]
	$Fe(acac)_3$	3.3	[26]
Dichloromethane	$Co(acac)_2py_2$	3.0	[32]
	$Co(acac)_2py_2$	3.7	[b]
	$Co(acac)_2(\gamma\text{-pic})_2$	2.3	[b]
	$Co(acac)_2(pipe)_2$	3.0	[29]
	$Cr(acac)_3$	2.0	[25]
Dichloroethane	$Cr(acac)_3$	2.4	[25]
Acetone	$Cr(acac)_3$	1.6	[25]
Trichloroethylene	$Cr(acac)_3$	0.36 [c]	[43]
Phenylacetylene	$Cr(acac)_3$	0.09 [c]	[44]
Benzene	$Cr(acac)_3$	0.06 [c]	[44]
Benzene	$Cr(acac)_3$	0.65	[25]
Benzene	$Co(acac)_2(pipe)_2$	0.2	[29]

[a] Accuracy of the measurement is about 40%. [b] Calculated from the data in [29] using formula (9). [c] Measured at large concentrations of the ligand where its self-association is possible.

TABLE 4

Stability constants (298 K) of outer-sphere complexes in carbon tetrachloride

Ligand 1	Metal complex 2	$\beta^{(H)}$ (l mol^{-1}) [a] 3	Ref. 4
Chloroform	$Co(acac)_3$	0.9	[52]
	$Co(acac)_3$	1.1	[b]
	$Cr(acac)_3$	0.9	[b]
	$Cr(acac)_3$	0.9	[25,43]
	$Cr(tfa)_3$	0.2	[25,43]
	$Fe(ba)_3$	0.5	[73]
	$Fe(btfa)_3$	0.2	[73]
	$Fe(acac)_3$	0.9	[73]
	$Fe(gfaa)_3$	< 0.05	[73]
	$Fe(dpm)_3$	< 0.05	[73]
	$Fe(pta)_3$	< 0.05	[73]
Dichloromethane	$Cr(acac)_3$	0.6	[25]
	$Cr(tfa)_3$	0.3	[25]
	$Cr(fod)_3$	0.1	[25]
	$Fe(acac)_3$	0.6	[25]

TABLE 4 (continued)

Ligand 1	Metal complex 2	$\beta^{(H)}$ (l mol^{-1})[a] 3	Ref. 4
	Fe(tfa)$_3$	0.3	[25]
	Fe(tfa)$_3$	0.2	[73]
	Fe(dbm)$_3$	0.6	[73]
	Cu(acac)$_2$	0.8	[25]
Dichloroethane	Cr(acac)$_3$	0.4	[25]
Trichloroethylene	Cr(acac)$_3$	0.14[c]	[43]
Methanol	Cr(acac)$_3$	1.3	[25]
	Cr(acac)$_3$	1.6	[47]
	Cr(tfa)$_3$	1.0	[25]
	Fe(acac)$_3$	1.1	[67]
3D-methanol	Fe(dbm)$_3$	0.9	[73]
	Fe(pta)$_3$	0.6	[73]
	Fe(btfa)$_3$	0.3	[73]
	Fe(tfa)$_3$	0.2	[73]
Ethanol	Cr(acac)$_3$	1.6	[47]
Isopropanol	Cr(acac)$_3$	1.1	[47]
n-Butanol	Cr(acac)$_3$	1.3	[47]
	Cr(acac)$_3$	0.9	[25]
	Fe(acac)$_3$	0.9	[67]
t-Butanol	Cr(acac)$_3$	0.9	[25]
	Cr(acac)$_3$	1.3	[47]
Acetonitrile	Cr(acac)$_3$	1.6	[25]
	Cr(tfa)$_3$	1.7	[75]
Methylisocyanide	Fe(acac)$_3$	0.6	[67]
Acetone	Cr(tfa)$_3$	1.0	[25]
	Cr(acac)$_3$	0.7	[25]
Toluene	Cr(acac)$_3$	0.2	[25]
Benzene	Cr(acac)$_3$	0.2	[25]
	Cr(tfa)$_3$	0.3	[25]
Pyridine	Co(acac)$_2$py$_2$	0.2	[56]
	Ni(acac)$_2$py$_2$	0.3	[56]
Acetic acid	Cr(acac)$_3$	1.3	[25]

[a] Accuracy of the measurement is ca. 40%. [b] Calculated from data in ref. 18. [c] Measured at large concentrations of the ligand.

List of abbreviations for Tables 3 and 4

H(acac), acetylacetone; H(ba), benzoylacetone; H(tfa), trifluoroacetylacetone; H(btfa), benzoyltrifluoroacetone; H(gfa), hexafluoroacetylacetone; H(dpm), dipivaloylmethane; H(pta), pivaloyltrifluoroacetone; H(fod), heptafluorobutanoylpivaloylmethane; H(dbm), dibenzoylmethane.

TABLE 5

Stability constants of various OSCs with Cr(acac)$_3$ in different solvents (298 K)

Ligand	Solvent	$\beta^{(C)}$ (l mol^{-1})[a]	Ref.
Chloroform	carbon tetrachloride	0.3	[43]
Carbon tetrachloride	cyclohexane	0.1	[81]
Benzene	cyclohexane	0.08	[44]
Toluene	cyclohexane	0.08	[44]
Phenylacetylene	cyclohexane	0.09	[44]
Pyridine	cyclohexane	0.17	[44]
Trichloroethylene	cyclohexane	0.36	[43]
Trichloroethylene	carbon tetrachloride	0.13	[43]
Methanol	carbon tetrachloride	1.3	[47]
Ethanol	carbon tetrachloride	1.3	[47]
Isopropanol	carbon tetrachloride	1.5	[47]
n-Butanol	carbon tetrachloride	1.5	[47]
t-Butanol	carbon tetrachloride	1.6	[47]

[a] Accuracy of the measurement is ca. 40%.

for the chemical shifts (δ) of ^{13}C nuclei of organic solvents.

As a typical example the concentration dependences for the paramagnetic contribution to the width of the NMR line and for the paramagnetic shift of ^{13}C nuclei of CHCl$_3$ in solutions containing Cr(acac)$_3$ are presented in Fig. 6 [43]. Both dependences are described well by formula (9) for $\alpha =$

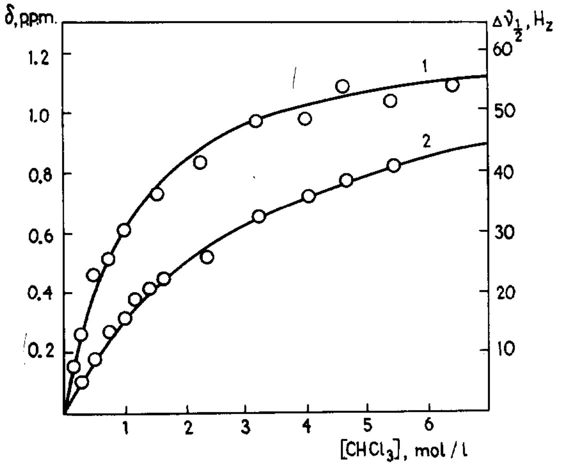

Fig. 6. The linewidth of the proton of the chloroform molecule (1) and paramagnetic shift of ^{13}C nucleus (2) vs. concentration of CHCl$_3$ in CCl$_4$ solution at a constant ratio $\alpha =$ [Cr(acac)$_3$]/[CHCl$_3$]; for curve (1) $\alpha_1 = 7.3 \times 10^{-3}$; for curve (2) $\alpha_2 = 1.53 \times 10^{-2}$. The upper boundary of the figure corresponds to the extreme values of $\alpha_1 N \delta^{(M)} = 1.3$ ppm and $\alpha_2 N \Delta \nu_{1/2}^{(M)} = 65$ Hz.

$[Cr(acac)_3]_0/[CHCl_3]_0 = \text{const}$, however they correspond to different values of the stability constant β. Indeed, by linearising these dependences in $\{\Delta\nu_{1/2}^{-1}, [CHCl_3]_0^{-1}\}$ and $\{\delta^{-1}, [CHCl_3]_0^{-1}\}$ coordinates we have determined $\beta^{(H)} = 0.9 \pm 0.3$ l mol^{-1} from the NMR linewidth of the $CHCl_3$ proton (the concentration dependence of parameter R_1 for this proton gives the same value of $\beta^{(H)}$ [25]), and $\beta^{(C)} = 0.30 \pm 0.02$ l mol^{-1} from the shift of ^{13}C nuclei of $CHCl_3$. As is expected, the value of product of the paramagnetic shift $\delta^{(M)}$ of ^{13}C nuclei of chloroform in the coordination sphere of the metal complex and the coordination number N of the OSC ($\delta^{(M)}N = 85 \pm 5$ ppm) coincides with the value of this product calculated from the earlier work [38]. The constant $\beta^{(H)}$ and the product of N and the paramagnetic contribution to the proton linewidth, ($N\Delta\nu_{1/2}^{(M)} = (8.9 \pm 0.4)10^3$ Hz) also coincide with the values measured earlier [25].

As has been shown in the previous section, the different values obtained for $\beta^{(C)}$ and $\beta^{(H)}$ suggest that the molecules of $CHCl_3$ form two types of outer-sphere adducts with the complex $Cr(acac)_3$, the parameters $\beta^{(C)}$ and $\beta^{(H)}$ corresponding to $CHCl_3$ coordination at different sites of the outer coordination sphere of $Cr(acac)_3$. Thus, variations in the proton relaxation rates and in ^{13}C chemical shifts can be accounted for by the formation of two different types of OSCs. Note that $\beta^{(H)} > \beta^{(C)}$, i.e. OSCs of the first type, formation of which is manifested in the change of R_1 and R_2 (and also of $\Delta\nu_{1/2}$) for the proton, are more stable than OSCs of the second type (see Table 5), formation of which is manifested in the change of chemical shifts of ^{13}C nuclei.

First consider the data on $\beta^{(H)}$. As is seen in Tables 3 and 4, the variation of $\beta^{(H)}$ for various metals and β-diketonate ligands is relatively small (one–two orders of magnitude only). Nevertheless, it is possible to distinguish certain tendencies. For the same outer-sphere ligand and for the same inner-sphere ligands, $\beta^{(H)}$ changes only slightly when the metal atom is changed. However $\beta^{(H)}$ is much more sensitive to the nature of the inner-sphere ligands. This seems to indicate that OSCs of the first type are produced, most probably, by the interaction of the outer-sphere ligands with the functional groups of the inner-sphere ligands rather than with the metal atom itself. This conclusion is not trivial because for the observed low heats of OSC formation (see below) one cannot exclude a priori the possibility of formation of OSCs due to a weak (because of a large distance between the outer-sphere ligand and the metal atom) direct overlapping of molecular orbitals of the outer-sphere ligands and of the metal.

Note also that the values of $\beta^{(H)}$ (Tables 3 and 4) do not correlate with the values of the dipole moment of the molecules. For example, $\beta^{(H)}_{CH_3OH} > \beta^{(H)}_{(CH_3)_2CO}$, whereas for the dipole moments of these molecules an inverse relation is valid. These data seem to contradict the conclusions [19–21] that non-specific electrostatic interactions are responsible for the formation of OSCs. A significant difference between the values of $\beta^{(H)}$ measured for the same OSC in cyclohexane and in CCl_4 should also be noted. A several fold decrease of $\beta^{(H)}$ upon transition from cyclohexane to CCl_4 as a solvent cannot be explained by the formation of associates between the outer-sphere ligand and CCl_4 via the second equation of Scheme (22). In fact, the known constants of association of L with CCl_4 [76,77] allow one to estimate $\beta^{(H)}$ for L + CCl_4 solutions using formula (23). Recall that the effective stability constant $\beta_{eff}^{(H)}$ given by this formula is just the value that takes into account the association of L with CCl_4. However, the values of $\beta_{eff}^{(H)}$ calculated in this way were found to differ from the true values of the stability constant $\beta^{(H)}$ only by 10%. This difference is significantly smaller than the typical variation of $\beta^{(H)}$ passing from cyclohexane as a solvent to CCl_4. Thus, the data seem to indicate that in contradiction of the assumptions which are sometimes expressed [78], CCl_4 molecules are not inert towards OSC formation and can compete with other organic molecules for the sites in the outer coordination sphere. The possibility of outer-sphere coordination of CCl_4 was also suggested in [21] and was supported later by observations of a high relaxation rate of ^{13}C nuclei for CCl_4 (in comparison with C_6H_{12}) in the presence of $Cr(acac)_3$ and $Fe(acac)_3$ [79,80]. Assuming that cyclohexane forms no OSCs, from comparison of $\beta^{(H)}$ values measured for OSCs of $Cr(acac)_3$ with various organic molecules in C_6H_{12} and CCl_4 (Tables 4 and 5) one can find via formula (15) that for $Cr(acac)_3$ in CCl_4 $\beta_S^{(H)} = 0.2 \pm 0.1$ l mol^{-1}. The value of $\beta_S^{(H)}$ estimated in this way coincides (within the error of the measurements) with the stability constant of the OSC between $Cr(acac)_3$ and CCl_4, $\beta^{(C)} = 0.10 \pm 0.02$ l mol^{-1}, measured later directly from the concentration dependence of the chemical shift of the ^{13}C nucleus of CCl_4 molecules [81]. Thus, the principal reason for the decrease of OSC stability constants upon transition from C_6H_{12} to CCl_4, indeed seems to be the competition between organic molecules and CCl_4 for coordination sites in the metal complex outer sphere.

At first glance it might seem puzzling that $\beta^{(H)}$ for ligands which are strong proton-donors, such as acetic acid and alcohols, exceeds only slightly $\beta^{(H)}$ for weak proton donors such as chloroform and methylene chloride. However, as shown by Kitaigorodskii [75], this fact is readily explained by a high degree of self-association of alcohols and acids. IR spectroscopy was employed [75] to measure β for OSCs formed by $Cr(acac)_3$ and methanol at low methanol concentrations ($[CH_3OH]_0 < 0.01$ mol l^{-1}) in a CCl_4 solution when the larger part of CH_3OH molecules is expected to be in the form of monomers [82]. The value of β was measured from the concentration dependences of the intensities of the OH-stretching (3670 cm^{-1}) band of the free methanol and of a new band at 3550 cm^{-1} which appeared upon addition of $Cr(acac)_3$ to $CH_3OH + CCl_4$ solution and was attributed to OSC formation. In agreement with expectation, the value $\beta = 4 \pm 1$ mol l^{-1} obtained for the monomeric form of CH_3OH is, indeed, significantly higher than that found at higher concentrations of methanol when self-association is expected to occur (see Table 4).

At this time the data on $\beta^{(C)}$ stability constants are less numerous than those on $\beta^{(H)}$. The available data on $\beta^{(C)}$ are compiled in Table 5. As follows from the table, $\beta^{(C)}$ is either far less than $\beta^{(H)}$ (e.g. for $CHCl_3$) or equal to $\beta^{(H)}$ (e.g. for alcohols). Note again that when $\beta^{(C)} \neq \beta^{(H)}$ one can state with certainty that at least two types of OSCs with different structures and stabilities are simultaneously formed. When $\beta^{(C)} = \beta^{(H)}$, the situation is less clear. Such a relationship between $\beta^{(C)}$ and $\beta^{(H)}$ can be due either to the presence in the solution of the same type of OSC whose formation can be determined both with ^{13}C NMR and ^{1}H NMR or to the presence of two or more different types of OSCs in the situation when formation of OSCs of one type excludes the possibility of formation of OSCs of another type.

Note also that the values of $\beta^{(C)}$ for OSCs formed by the same inner-sphere complex, $Cr(acac)_3$, with the molecules of quite different nature (CCl_4, C_6H_6 and pyridine) are approximately the same. This seems to indicate that similar interactions are responsible for the formation of OSCs with all these compounds. The structure of OSCs of different types will be considered in more detail in Section E.

(iv) Enthalpies and entropies of formation of outer-sphere complexes

In conformity with the low OSC stability constants, enthalpies and entropies of their formation are also relatively low, which is typical for associates formed in liquids via weak intermolecular interactions.

It was found for OSCs of $CHCl_3$ with Co(III) and Cr(III) acetylacetonates that $\Delta H^{(0)} = -2.3$ kcal mol^{-1}, $\Delta S^{(0)} = -4.7$ e.u. in benzene [18]. For OSCs of $Co(HB(pz)_3)_2$ with various organic compounds the enthalpies found from the temperature dependences of the chemical shifts caused by the formation of OSC are as follows: -2.9 kcal mol^{-1} (pyridine), -2.4 kcal mol^{-1} (aniline) [19] and -3.6, -2.2, -2.6 kcal mol^{-1} for $-CF_3$, $-OCH_3$ and $-N(CH_3)_2$ *para*-substituted anilines [20]. Such values of $\Delta H^{(0)}$ seem to be quite reasonable. Note that the values of $\Delta H^{(0)}$ were determined in [19,20] not from the temperature dependence of the stability constants but from the temperature dependence of the experimentally observed paramagnetic shifts on the assumption of the simplest (Curie law) temperature dependence for the paramagnetic shifts of the ligands in OSCs. Though being acceptable for $Co(HB(pz)_3)_2$, this assumption when applied to other complexes of Co(II) can, perhaps, lead to appreciable errors in $\Delta H^{(0)}$ since these complexes are known [31] often to demonstrate paramagnetic shift temperature dependence which is more complicated than the Curie law.

OSCs of phenol and of its sulfur- and selenium-containing analogs with tetrahedral M-chelates (M = Zn(II), Co(II), Ni(II), Cu(II); chelate = 1-methyl-2-phenyl-4-phenylaminomethylene-5-pyrrolate, 2-methyl-2-chloro-3-formyl-4-phenylaminomethylene-5-pyrrolate) have been studied by IR spectroscopy [83]. The enthalpy of OSC formation was found to vary from -1 to -8 kcal mol^{-1} depending on the nature of the heteroatom in the outer-sphere ligand and decreasing in the series O > S > Se. It depends also on the nature of the metal atom, decreasing in the series Cu(II) > Ni(II) > Co(II) > Zn(II). Moreover, the trends of the enthalpy and entropy change in these series are of the same character, i.e. a compensation effect is observed.

Surprisingly high values of enthalpy, $\Delta H^{(0)} = -(10\text{–}12)$ kcal mol^{-1} and entropy, $\Delta S^{(0)} = -(35\text{–}40)$ e.u. for the formation of OSCs between $Co(acac)_2py_2$ and $CHCl_3$, as well as CH_2Cl_2 molecules were reported in [28]. Since such high heat effects of OSC formation were not observed in other cases this system was later examined more thoroughly to elucidate the nature of its unique behavior [32]. The reason for the high heat effects was found to be the more complex character of $CHCl_3$ and CH_2Cl_2 outer-sphere coordination to $Co(acac)_2py_2$ compared with that assumed in [28]. It has been found [32] that, along with coordination in the region of the equatorial plane via the formation of hydrogen bonds with the oxygen atoms of chelate ligands, molecules of $CHCl_3$ and CH_2Cl_2 can also produce OSCs via interactions with the π–systems of the inner-sphere ligand. The OSC stability constant of the second type is rather low (0.15 l mol^{-1}). However, neglecting the contribution from OSCs of this type to the experimentally observed chemical shifts leads to appreciable errors in estimating $\beta^{(H)}$. By taking into account the formation of OSCs of the second type [32], the usual values: $\Delta H^{(0)} = -4.5 \pm 1.0$ kcal mol^{-1}, $\Delta S^{(0)} = -17 \pm 4$ e.u. and $\Delta H^{(0)} = -3.5 \pm 1.0$ kcal mol^{-1}, $\Delta S^{(0)} = -12 \pm 4$ e.u. have been obtained for the enthalpies and entropies of formation of the OSCs of the first type where $CHCl_3$ and CH_2Cl_2 molecules are bound to the inner-sphere ligands via hydrogen bonds. For OSCs formed by tetra-*p*-tolyl-porphyrinate Co(II) and 1,3,5-trinitrobenzene at the expense of the π–π interaction of the porphyrin ring with the outer-sphere ligand the values $\Delta H^{(0)} = -5.7 \pm 0.4$ kcal mol^{-1} and $\Delta S^{(0)} = -14 \pm 2$ e.u. were found [48].

Heat effects for the formation of OSCs between various transition metal β-diketonates and a variety of organic molecules have also been measured [25,75]. For all OSCs studied the heat effects and variations in entropy were found to be $\Delta H^{(0)} = -(2\text{–}5)$ kcal mol^{-1} and $\Delta S^{(0)} = -(5\text{–}15)$ e.u.

It follows from the above data that the energy of the outer-sphere ligand binding with metal complexes is usually about 2–5 kcal mol^{-1}, i.e. is rather low. However, since the outer coordination sphere can include several molecules, the total energy of OSC formation can be several times higher. For example, in the case of tris-β-diketonates of metals when three ligands can be added to the outer coordination sphere, this energy is expected to be about 6–15 kcal mol^{-1} which is not so small.

C. LIFE TIMES OF OUTER-SPHERE COMPLEXES

Life times of the OSCs can be determined from the analysis of the dependence of the rates of paramagnetic relaxation of the nuclei of molecules coordinated in the outer sphere on the electron resonance frequency. For magnetically isotropic complexes, the dipole–dipole contribution to the rate of spin-lattice relaxation, R_1, is described by the Solomon–Blombergen–Morgan equation [84–86]

$$R_1^{(M)} = 2/15\gamma_I^2\gamma_S^2\hbar^2S(S+1)\left(3\tau_C + \frac{7\tau_C}{1+\omega_S^2\tau_C^2}\right)\langle r^{-6}\rangle \tag{27}$$

In this equation γ_I and γ_S are magnetogyric ratios for the nucleus and electron respectively; S is the total electron spin of the complex; r is the distance between the nucleus and the metal atom averaged over all their mutual positions; ω_S is the electron resonance frequency. The correlation time, τ_C, is expressed through the relaxation time of the electron spin, τ_S, the correlation time of rotational diffusion, τ_r, of the complex and the life time, τ_h, of the nucleus in the coordination sphere of the complex as follows [87]:

$$\tau_C^{-1} = \tau_r^{-1} + \tau_S^{-1} + \tau_h^{-1} \tag{28}$$

For the strongly bound ligands, the time τ_h is large, so that τ_h^{-1} makes a small contribution to τ_C^{-1}. However, for labile ligands, in particular for outer-sphere ones, τ_h is comparable with τ_r and τ_S. By comparing the values of τ_C obtained from the dependences of $R_1^{(M)}$ on the frequency ω_S for the nuclei of stable and labile ligands of a given complex, one can find the life time τ_h of labile ligands in the coordination sphere of the metal atom.

This approach was used to determine τ_h for a series of organic ligands which form OSCs with paramagnetic complexes Fe(acac)$_3$ and Cr(acac)$_3$ [51,75]. The data obtained are listed in Table 6.

If the value of τ_r for strongly bound inner sphere ligands is known, τ_h for outer-sphere ligands can be measured in another, more simple way. This is based on a comparison of the rate of paramagnetic relaxation of protons of outer-sphere ligands with the rate of the quadrupole relaxation of deuterium nuclei of the same but deuterated ligands [52].

The relaxation rate of deuterium nuclei of ligands of paramagnetic com-

TABLE 6

Life times (300 K) of outer-sphere ligands in the coordination sphere of metal complexes

Metal complex	Outer-sphere ligand	$10^{11}\ \tau_h$(s)	Refs
$Cr(acac)_3$	chloroform	2.8 ± 0.5	[51]
$Cr(acac)_3$	dichloromethane	3.0 ± 0.6	[75]
$Cr(acac)_3$	acetonitrile	3.3 ± 1.0	[75]
$Cr(acac)_3$	acetone	3.7 ± 1.0	[75]
$Cr(acac)_3$	methanol	$5\ ^{+4}_{-1}$	[75]
$Cr(acac)_3$	trichloroethylene	3.0 ± 0.6	[43]
$Cr(acac)_3$	toluene	7 ± 2	[a]
$Cr(acac)_3$	pyridine	5 ± 2	[a]
$Fe(acac)_3$	chloroform	5.3 ± 1.0	[51]
$Fe(acac)_3$	acetonitrile	3.7 ± 1.0	[75]
$Fe(acac)_3$	methanol	$\geqslant 8$	[75]
$Co(acac)_3$	D-chloroform	8 ± 2	[52]

[a] Calculated from data in [44] according to [52].

plexes is determined by the sum of the two main contributions: from paramagnetic and from quadrupole interactions [88]. The paramagnetic contribution can easily be estimated from that for protons by taking into account the difference in magnetogyric ratios for hydrogen and deuterium nuclei. Consequently, for the quadrupole contribution $R_{1,Q}^{(M)}$ to the relaxation rate of deuterium one has

$$R_{1,Q}^{(M)} = R_1^{(M)}(D) - (\gamma_D/\gamma_H)^2 R_1^{(M)}(H) \tag{29}$$

Here, as in previous sections, the upper index (M) denotes parameter R_1 for protons (H) or for deuterium nuclei (D) of the ligand molecule when it is located in the coordination sphere of the metal complex; γ_D and γ_H stand for the magnetogyric ratio for the deuterium nucleus and proton, respectively.

The value of $R_{1,Q}^{(M)}$ is described by the formula [88]

$$R_{1,Q}^{(M)} = \frac{3\pi^2}{10} \cdot \frac{2I+3}{I^2(2I-1)} \cdot \left(\frac{e^2Qq}{h}\right)^2 \tau_C \tag{30}$$

where $I = 1$ is the nuclear spin of deuterium, eQ is its quadrupole moment (e is the electron charge); eq is the gradient of the electric field at the point where the deuterium nucleus is located. If the value of $(e^2Qq/h)^2$ is known, it is possible to calculate from eqn. (30) the value of τ_C and then of τ_h. The values of τ_h found from the rates $R_{1,Q}^{(M)}$ measured directly for diamagnetic complex $Co(acac)_3$ [52] and obtained from the comparison of the rates of paramagnetic and quadrupole relaxations for paramagnetic complex

$Cr(acac)_3$ [43] are also given in Table 6. It is seen in the Table that for all OSCs studied to date the life times are short and are within the interval 10^{-10}–10^{-11} s. Also it is seen that when passing from $Cr(acac)_3$ to $Fe(acac)_3$ and $Co(acac)_3$, the value of τ_h increases somewhat whereas the stability of OSC formed by chloroform with these complexes is nearly the same (see Tables 3 and 4). At present the reason for this effect is not clear. It cannot even be excluded that the observed increase in τ_h is not true, but reflects the errors of the measurement. Nevertheless, there seems to be no doubt that the order of magnitude of $\tau_h \simeq 10^{-10}$–10^{-11} s has been determined correctly.

The data allow one also to estimate the activation energy for the processes of OSCs dissociation. The life time of the ligand in the metal atom coordination sphere is related to the OSC dissociation constant through the formula $\tau_h = k_d^{-1}$. For the typical value of the preexponential factor for unimolecular reaction of 10^{13} s^{-1}, one obtains from the data in Table 6 for $CHCl_3$ molecule dissociation from the outer coordination spheres of $Cr(acac)_3$, $Fe(acac)_3$ and $Co(acac)_3$ the activation energies, $E_a = 3.4$ kcal mol^{-1}, 3.8 kcal mol^{-1} and 4.0 kcal mol^{-1}, respectively. Note that the values of E_a obtained are close to the enthalpies of OSC formation as is expected for processes of this type.

The temperature dependence of the NMR linewidths of benzene, acetonitrile, dimethylsulfoxide and methanol in solutions containing $Cr(acac)_3$ has been examined [89]. The linewidth $\Delta\nu_{1/2}$ is described by the formula $\Delta\nu_{1/2} = \Delta\nu_{1/2}^{*} \exp(-\Delta H^{\neq}/RT)$ with the effective activation enthalpies listed in Table 7. It follows from the previous section that in pure liquids used [89] as solvents, the equilibrium (1) must be shifted toward the right-hand side. Under these conditions the linewidth of the solvent can be described as $\Delta\nu_{1/2} = \Delta\nu_{1/2}^{(M)} N [\mathrm{Cr(acac)_3}]_0 [\mathrm{L}]_0^{-1}$, where $\Delta\nu_{1/2}^{(M)}$ is the linewidth for the solvent molecule in the complex. Since the value of $\Delta\nu_{1/2}^{(M)}$ is proportional to τ_C [87], the temperature dependence observed [89] reflects the temperature dependence of the correlation time for the dipole interaction, τ_C. In turn, τ_C depends not only on the life time of OSC, τ_h, but also on the time

TABLE 7

Effective enthalpy of activation for variations in PMR linewidths of different solvents in the presence of $Cr(acac)_3$ [89]

Solvent	$\Delta H^{\neq}$ (kcal mol^{-1})
Acetonitrile	2.44
Benzene	2.96
Dimethylsulfoxide	3.41
Methanol	2.5 (OH) 3.16 (CH_3)

of the diffusional rotation of the complex, τ_r, on the time of electron relaxation, τ_S (see formula (28)), as well as on the rate of the intramolecular rotation of the functional groups of the outer-sphere ligand. Therefore the data in Table 7 can be regarded only as estimates of activation enthalpies for OSC dissociation. This is also indicated by the difference in $\Delta H^{\neq}$ values determined from the linewidths of different (OH and CH_3) protons of the same substance, namely methanol.

Note that the OSC life times of about 10^{-11}–10^{-10} s are in agreement with the life times measured independently for other types of weak associates in solution. For examples, from the rates of the quadrupole relaxation of the deuterium nucleus the life time of the hydrogen bond between oxygen atoms of polyvinylpyrrolidone and the $CDCl_3$ deuterium atom was found to be about 4.5×10^{-11} s [90]. The life times of molecular complexes of nitroxide radicals with proton-donor molecules of the solvent ($(3–6) \times 10^{-11}$ s) have been measured by NMR [91–93].

The life time of molecules in the outer coordination sphere of metal complexes is close to the typical life times of diffusion pairs in liquid. However there is an important difference between diffusion pairs and the outer-sphere complexes discussed here. In diffusion pairs the colliding molecules are oriented randomly with respect to each other, whereas in the outer sphere of metal complexes the ligand molecules have a distinct preferred orientation (see the next Section).

D. GEOMETRICAL STRUCTURE OF OUTER-SPHERE COMPLEXES

Considerable changes in chemical shifts and relaxation rates of outer-sphere ligand nuclei in paramagnetic metal outer-sphere complexes can be used to find some parameters that characterize their geometrical structure.

(i) Interrelationship between geometrical characteristics and NMR parameters of outer-sphere complexes

The paramagnetic contribution to the rate of spin–lattice relaxation, $R_1^{(M)}$, is determined by three main types of interaction: (i) dipole–dipole interaction between magnetic moments of the nucleus and metal atom; (ii) Fermi-contact interaction of the nuclear magnetic moment with the spin density on the *s*-orbital of the same nucleus, and (iii) dipole–dipole interaction of the nuclear magnetic moment with the spin density on *p*-orbitals of the same nucleus and on the orbitals of neighbouring atoms of the ligand. If the contribution (i) to $R_1^{(M)}$ predominates over the contributions (ii) and (iii), the values of $R_1^{(M)}$ can be used to analyze the geometrical structure of the metal complex proceeding from formulae of the type (27).

The contribution of interaction (ii) to $R_1^{(M)}$ is customarily smaller than the contributions of (i) and (iii), provided that the inequality $\omega_s \tau_s \gg 1$, where ω_s is the precession frequency of the electron spin of the complex, is satisfied (for more details see refs. 56 and 87). In modern NMR spectrometers, magnetic fields of 7 T or higher are used. For these fields $\omega_s > 1.2 \times 10^{12}$ rad s^{-1}. For most transition metals, but excluding Co(II) octahedral complexes, $\tau_s > 10^{-11}$ s [87], i.e. the contact contribution to the relaxation rate can be neglected.

As for the contribution of interaction (iii) to $R_1^{(M)}$, it is usually small for ligand protons [94–105]. However, for ^{13}C nuclei, the relative role of this contribution, $R_1^{(L)}$, can be different. For some compounds it is predominant [94–100], yet being very small for many other metal complexes [30,56,101–105]. According to [94], $R_1^{(L)}$ is proportional to the square of the spin density on the ligand orbitals. Therefore, one might expect a certain correlation between $R_1^{(L)}$ and contact paramagnetic shifts which are proportional to the first power of the spin density delocalized on the ligand. For pyridine [106] a clear qualitative correlation has been observed between $R_1^{(L)}$ for ^{13}C nuclei of the molecule of the inner-sphere ligand and its coordination type with Cu(II). When pyridine is coordinated towards the *d*-orbital of Cu(II) which has an unpaired electron, large contact paramagnetic shifts $\delta^{(C)}$ and $\delta^{(H)}$ and high $R_1^{(L)}$ are observed. On the contrary, if pyridine interacts with the *d*-orbital free of unpaired electrons, which is for example the case for the axial adduct $Cu(acac)_2py$, the shifts are approximately one order of magnitude less, and contributions of $R_1^{(L)}$ to $R_1^{(M)}$ are negligibly small.

Thus, for the preliminary estimation of the magnitude of contributions $R_1^{(L)}$ one can use the values of the shifts $\delta^{(C)}$ and $\delta^{(H)}$ measured for various ligand nuclei of the complex under study. Since paramagnetic shifts measured for various nuclei of OSC ligands usually do not exceed those for pyridine nuclei in the complex $Cu(acac)_2py$ one can expect that for most OSCs studied, this contribution will be small.

The value of the dipole–dipole contribution (i) for magnetically isotropic complexes is described by formula (27). It follows from this formula that if correlation times, τ_C, are known, it is possible to calculate from values $R_1^{(M)}$ a mean distance between nuclei of the outer-sphere ligand and the metal atom and, thus, to determine the position of the ligand with respect to the metal atom.

The paramagnetic shifts, $\delta^{(M)}$, which arise upon ligand insertion into a magnetically anisotropic complex, also depend on the OSC geometrical parameters. For example, for the pseudocontact (dipole–dipole) component $\delta_{P.C.}^{(M)}$, in the case of axially symmetric complexes the following expression is valid [31]

$$\delta_{P.C.}^{(M)} = \frac{\beta^2 S(S+1)}{9kT}\left(g_\parallel^2 - g_\perp^2\right)\left\langle \frac{1 - 3\cos^2\theta}{r^3} \right\rangle \tag{31}$$

where r is the distance between the metal and the ligand nucleus; θ is the angle between the principal axis of magnetic anisotropy of the complex and the direction of vector $\bar{r}$; $g_{\parallel}$ and $g_{\perp}$ are respectively the parallel and perpendicular components of an effective [56] g-tensor of the complex; k is the Boltzmann constant; T is the temperature in K.

The values of $\delta^{(M)}$ can, in principle, also include the contact terms resulting from delocalization of spin density transferred from the metal atom on the nucleus of the outer-sphere ligands [31,88]. In contrast to $R_1^{(M)}$ for which these contributions are usually small, for $\delta^{(M)}$ they can be high.

(ii) Geometrical structure of outer-sphere complexes as suggested by NMR data

Relaxation rates, linewidths and chemical shifts were used by many authors to determine the orientation of outer-sphere ligands. For example, in the presence of $Cr(acac)_3$ the broadening of the line $\Delta\nu_{1/2}$ observed experimentally for protons of the hydroxyl group of methanol is 2.4 times larger than that for CH_3 protons, which indicates that the hydroxyl group of MeOH in OSC is oriented toward the metal atom [17].

For aniline, the paramagnetic shifts of protons decrease in the order $NH_2 > o\text{-H} > m\text{-H} > p\text{-H}$ in the presence of $Co(HB(pz)_3)_2$ whereas for pyridine protons, by contrast, the largest shift has the proton which is most remote from the nitrogen atom: $p\text{-H} > m\text{-H} > o\text{-H}$ [19]. Such an order of variation in $\delta^{(M)}$ suggests that in the coordinated aniline molecule a nitrogen atom is directed toward the center, whereas the reverse is true for the pyridine molecule. Based [22,23] on the character of the magnetic anisotropy of the complex and on the observation that NMR signals of aniline and pyridine protons are shifted toward a strong field, these ligands lie on the plane perpendicular to the symmetry axis of the complex [19]. This conclusion [19] is in agreement with the results in ref. 56 which prove that in OSCs with $Co(acac)_2py_2$ and $Ni(acac)_2py_2$, the molecules of pyridine are also oriented by p-protons toward the Co(II) and Ni(II) atoms.

From comparison of $\delta^{(M)}$for ^1H and ^{13}C nuclei of $CHCl_3$ molecules in the presence of $Co(acac)_2py_2$ it has been shown that molecules of $CHCl_3$ coordinated in the outer sphere are located predominantly near the equatorial plane of $Co(acac)_2py_2$, their protons being directed toward the Co(II) atom [28]. In this case the distance between the Co(II) atom and the H atom of $CHCl_3$ is 3.7 Å. This result is in agreement with the distances (4.0 ± 0.2 Å) between the hydrogen atoms of $CHCl_3$ and CH_2Cl_2 molecules coordinated in the outer sphere and Co(II) atom of $Co(acac)_2py_2$ which were estimated later from the analysis of the linewidths of these protons [29].

Using the paramagnetic shifts and relaxation rates of protons of 1,3,5-trinitrobenzene (TNB) which makes an outer-sphere complex with tetra-p-

tolylporphyrin Co(II), the plane of the TNB aromatic ring is parallel to that of the porphyrin ring, the distance between these planes being equal to 3.2 ± 0.2 Å [48].

In the case of outer-sphere complexes of TNB with high-spin adducts of *p*-substituted tetraphenylporphyrin Fe(III) having a Cl^- anion, the molecule of TNB is at a distance of 3 Å from the porphyrin plane and is at the opposite side of the complex with respect to the axial ligand Cl^-. The centre of the molecule of TNB is approximately above the pyrrole nitrogen, and the NO_2-groups are directed away from Fe(III) [107].

Based on the measurements of relaxation rates of protons of hydroxyl and alkyl groups of methyl, *n*-butyl, *t*-butyl alcohols and acetic acid, it has been established that in OSCs with transition metal *β*-diketonates, the H atom of the hydroxyl group of these molecules is directed toward the metal atom. Methyl groups of methylisocyanide molecules in an OSC with $Fe(acac)_3$ were found to be directed toward the Fe(III) atom [67].

The conclusions concerning the direction of predominant orientation of the outer-sphere ligands in the coordination sphere of OSCs appear to be reliable. At the same time, the calculations of the interatomic distances in OSCs should be regarded as rather approximate because of numerous assumptions concerning magnetic and geometrical structures of the initial metal complexes, of the composition and stability of OSCs, etc. which were often made when calculating interatomic distances from NMR data. In fact, it is seen from the data presented above that for calculation of the value of r from R_1 it is necessary to find, first of all, $R_1^{(M)}$, i.e. the nucleus relaxation rate in the coordination sphere of OSC. To find $R_1^{(M)}$, as follows from eqn. (9), the coordination number of the OSC must be known. For subsequent calculation of r from $R_1^{(M)}$ via formula (27), it is necessary to determine the g-factor of the complex and the correlation time τ_C. The value of the g-factor can be measured by ESR technique and the value of τ_C from ESR and NMR spectra.

The data on the composition of OSCs and their life times presented in the previous sections permit one to get rid of some uncertainties mentioned above and provide the possibility of estimating more accurately the OSC geometrical parameters. The distance between the metal atoms of $Cr(acac)_3$ and $Fe(acac)_3$ and the nuclei of the outer-sphere ligands found from $R_1^{(M)}$ using experimental values of N, g, τ_r, τ_s and τ_h [26] are compiled in Table 8. Experimental values of R_1, as well as values of τ_C used for the calculation of r also are listed in the table.

The distances, r, obtained seem to be quite reasonable. Indeed, if the distance between the oxygen atom of acetylacetonate and the proton of the outer-sphere ligand L is assumed to be about 1.8–2.0 Å (typical values for the lengths of hydrogen O...H bonds [82]), then, depending on the orientation of L, we may expect the distance between the proton of L and the metal atom to be within the range 3.0–3.7 Å, which is close to the values listed in Table 8. For protons of acetone and acetonitrile the distance is appreciably larger, which indicates the differing ways of coordination of these molecules from those of alkylhalides and alcohols.

Note also that the values of r listed in Table 8 and calculated using experimental coordination numbers N and life times τ_h of OSCs do not differ so greatly from the values found in earlier works where N and τ_h were not measured at all. A reason for this is that the experimental values of N have the same order of magnitude as those used in earlier works and the life times of OSCs have nearly the same order of magnitude as have the rotation correlation times of complexes, τ_r, which were taken as τ_C in these studies. Since for the calculation of r the root to the 6th power is extracted from $R_1^{(M)}$, N and τ_C (see formula (27)), even a several hundred percent error in the values of all these parameters has a relatively small influence on r. For example, a two-fold change in $R_1^{(M)}$, N or τ_C leads to the change of r only by 12%.

Note also an appreciable (beyond the measurement error) difference in r for protons (and for carbon atoms) of different outer-sphere ligands which

TABLE 8

Correlation time τ_C and distance r between metal atoms and ligand nuclei in outer-sphere complexes [26]

Metal complex	Outer-sphere ligand	$10^{11}\ \tau_C$ (s) [a]	R_1 (Hz) [b]	r (Å)
$Cr(acac)_3$	chloroform	1.8	170 (H)	3.14 ± 0.15
			2.4 (^{13}C)	4.05 ± 0.35
	methanol	2.8	330 (H)	3.65 ± 0.25
			56 (CH_3)	4.90 ± 0.50
	dichloromethane	1.7	35 (H)	3.95 ± 0.25
	acetonitrile	2.0	37 (H)	4.63 ± 0.40
	acetone	2.1	13 (H)	5.72 ± 0.50
	trichloroethylene [c]	2.0	6300 (CClH)	3.25 ± 0.15
			130 (^{13}CClH)	3.9 ± 0.2
			43 ($^{13}CCl_2$)	4.7 ± 0.4
$Fe(acac)_3$	chloroform	2.0	280 (H)	3.39 ± 0.17
	methanol	3.0	670 (H)	3.80 ± 0.30
			122 (CH_3)	5.05 ± 0.55
	acetonitrile	1.8	64 (H)	4.82 ± 0.45

[a] Values of τ_C for the field of 2.1 T.

[b] Values of R_1 for 0.1 mol l^{-1} $Cr(acac)_3$ and $Fe(acac)_3$.

[c] Values of R_1 correspond to the relaxation in the coordination sphere of $Cr(acac)_3$ [43].

make OSCs of the same type (via hydrogen bonds). One of the reasons for this effect is that the contribution to R_1 from the coordination of $CHCl_3$, CH_2Cl_2 and CH_3OH in the outer sphere, other than the predominant coordination via formation of hydrogen bonds, is not taken into account. Being less stable than OSCs with hydrogen bonds, those formed at the expense of other types of interactions may not reveal themselves in the measurements of coordination numbers and stability constants of OSCs with hydrogen bonds, nor in the study of the preferential orientation of outer-sphere ligands carried out at low enough concentrations. However, it cannot be excluded that they manifest themselves to a larger extent in the measurements of the absolute values of parameters $R_1^{(M)}$ and $\delta^{(M)}$. This situation will be illustrated in the next section.

However, we cannot exclude yet another possibility, namely, that the differences discussed in r values for the OSCs of metal complexes with $CHCl_3$, CH_2Cl_2 and CH_3OH reflect real differences in the structure of OSCs with these ligands. Additional investigation is needed to clarify this problem.

Finally, we consider the data on paramagnetic shifts and relaxation rates of nuclei of aromatic molecules in the outer coordination sphere of $Cr(acac)_3$ presented in Tables 9 and 10. Table 9 also gives the mean distances from the atoms of outer-sphere ligands to the atom of Cr(III) calculated from $R_1^{(M)}$. Note, first, an approximate constancy of the ratios of paramagnetic shifts of

TABLE 9

Relaxation rates, $R_1^{(M)}$ (s^{-1}, above the line) and corresponding distances, r (Å, under the line), for nuclei of aromatic molecules in OSCs with $Cr(acac)_3$ calculated for $N = 3$ (see text). [a] $T = 300$ K

Nucleus	Benzene	Toluene	Phenylacetylene	Pyridine
$^{13}C1$		$\frac{34}{5.3}$	$\frac{42}{5.2}$	
$^{13}C2$	$\frac{89}{5.1}$	$\frac{65}{4.8}$	$\frac{50}{5.0}$	$\frac{40}{5.1}$
$^{13}C3$		$\frac{68}{4.8}$	$\frac{57}{4.9}$	$\frac{70}{4.6}$
$^{13}C4$		$\frac{117}{4.3}$	$\frac{53}{5.0}$	$\frac{74}{4.6}$
$^{13}CH_3$		$\frac{32}{5.4}$		
$\overset{13}{-}C{\equiv}C{-}H$			$\frac{53}{5.0}$	
$-C{\equiv}^{13}C{-}H$			$\frac{116}{4.4}$	
$^1H2$		$\frac{1380}{4.6}$	$\frac{1050}{4.8}$	$\frac{1260}{4.5}$
$^1H3$	$\frac{1750}{4.9}$			$\frac{2270}{4.1}$
$^1H4$		$\frac{1890}{4.3}$	$\frac{1340}{4.6}$	$\frac{2020}{4.2}$
C^1H_3		$\frac{990}{4.8}$		
$-C{\equiv}C{-}^1H$			$\frac{5270}{3.7}$	

[a] The error is 10% for R_1 and 5% for r.

TABLE 10

Paramagnetic shifts[a] (ppm) of nuclei of aromatic molecules in OSCs with $Cr(acac)_3$, calculated for $N = 3$ (see text)

Nucleus	Benzene	Toluene	Phenylacetylene	Phenyliso-cyanide	Pyridine
$^{13}C_1$		2.8(4)	1.5(2)	3.7(4)	
$^{13}C_2$	−10.8(4)	−7.0(4)	−4.0(5)	−10.6(4)	−9(2)
$^{13}C_3$		−9.9(4)	−7.7(5)	−17.3(4)	−14(2)
$^{13}C_4$		−12.6(4)	−7.7(5)	−15.3(4)	−15(2)
$^{13}CH_3$		−14.2(12)			
$-^{13}C{\equiv}C{-}H$			−7.3(8)		
$-C{\equiv}^{13}C{-}H$			−35(4)		
^{1}H	−0.4(1)				
^{14}N					−20(4)

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[a] The error of the last figure is given in parentheses.

the ^1H and ^{13}C nuclei in *ortho, meta* and *para* positions of the aromatic rings of all substituted benzenes and of pyridine. This constancy indicates a similar character of interactions responsible for the formation of OSCs for all these substances. Most probably this is a donor–acceptor interaction

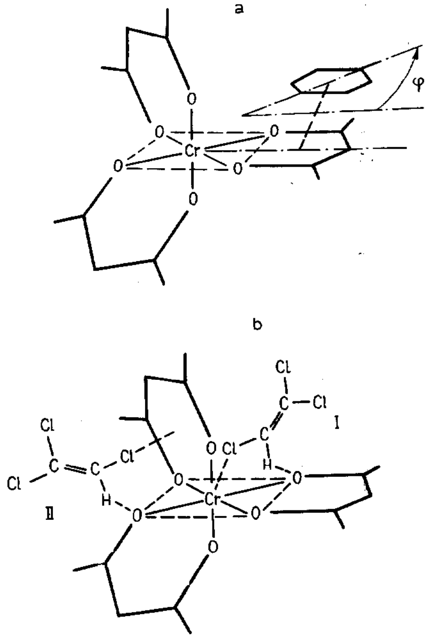


Fig. 7. The proposed structure of the outer-sphere complexes of $Cr(acac)_3$ with toluene (a) and C_2HCl_3 (b).

between π-systems of the aromatic molecule and the β–diketonate ligand. This conclusion is in agreement with the data on the mean distances r between atoms of outer-sphere ligands and the metal atom.

As is seen in Table 9, for all C–H fragments of aromatic molecules $r_H < r_C$. Such a ratio corresponds, for example, to the structure of an OSC in which the aromatic molecule can rotate around the axis perpendicular to the plane of the aromatic ring, resulting in the formation of a set of similar OSCs characterized by different angles ϕ (see Fig. 7a). Since $R_1^{(M)}$ decreases very quickly as the distance between the nucleus and the metal atom increases, the main contribution to $R_1^{(M)}$ will be made by those ligand orientations in which r is a minimum. Within the coordination model discussed, the values of r calculated from $R_1^{(M)}$ do correspond to such orientations. It is seen in Fig. 7a that upon rotation the shortest possible distance between the metal atom and the proton of the C–H fragment is, indeed, somewhat smaller than that for carbon nuclei.

Note also rather large paramagnetic shifts and short distances r observed for the nuclei of the acetylene groups of phenylacetylene. This fact can be explained as follows. Along with the coordination via the aromatic ring, there occurs also coordination of this substance through π-orbitals of the acetylene fragment and/or via the formation of hydrogen bonds between the relatively acidic proton of the acetylene group and the oxygen atom of the β-diketonate ligand, likewise in the case of chloroform molecule.

E. THE NATURE OF OUTER-SPHERE COORDINATION BONDS

(i) Interactions responsible for the formation of outer-sphere complexes

It follows from the above data that there are at least three types of interactions responsible for the formation of OSCs between electrically neutral metal complexes and solvent molecules. They are (i) formation of hydrogen bonds, (ii) donor–acceptor interactions involving molecular orbitals of inner-sphere ligands, and (iii) electrostatic interactions of solvent dipoles with non-compensated charges of the metal complex atoms. One more type of interaction which may also lead to the formation of OSCs are (iv) interactions resulting from the direct overlap of the orbitals of the metal atom and of an atom of the outer-sphere ligand (see below).

Formation of an OSC via hydrogen bonds between oxygen atoms of inner-sphere ligands and hydrogen atoms of the solvent molecules has been observed many times by IR [14–16,75], NMR [13,17,18,24–30] and ESR [50,108] methods.

Examples of OSCs formed by donor–acceptor interactions involving π-systems include complexes of trinitrobenzene with Co(II) porphyrin [48,49] and Fe(III) porphyrins [107] and evidently, by $CHCl_3$–$Co(acac)_2py_2$ complexes produced via addition of $CHCl_3$ molecules to the π-system of the inner-sphere ligands in solutions with a high concentration of $CHCl_3$ [32].

$Co(HB(pz)_3)_2$, for which a correlation between the OSC stability constants and dipole moments of outer-sphere ligands has been found [19–21], appears to be a metal complex which makes OSCs mostly via the electrostatic interactions.

The same metal complex may interact with various ligands producing OSCs of various types. As an example, consider OSCs formed by electrically neutral transition metal β-diketonates. Stability constants for these OSCs are compiled in Tables 3 and 4, and distances between the metal atoms and ligand atoms in Table 8. It follows that ligands which make OSCs with β–diketonates fall into two groups: group A (chloroform, alcohols, acetic acid, methylene chloride, dichloroethane) which are proton donors and group B (acetone, benzene, toluene, acetonitrile) which provide the role of proton acceptors in the formation of hydrogen bonds [82]. These two groups of ligands are characterized by different coordination mechanisms. This conclusion is supported by the following facts. First, upon substitution of methyl groups in a chelate ring by more electronegative groups containing fluorine atoms, $\beta^{(H)}$ decreases notably for group A ligands and increases somewhat for group B ligands (Tables 3 and 4). Second, the relaxation rate $R_1^{(M)}$ of protons of molecules of group A is significantly higher than that of groups B (Table 8). These facts can easily be explained if one assumes that molecules A form hydrogen bonds with oxygen atoms of the chelate ring of the metal complex while molecules of group B interact with the π-system electron of the chelate playing the role of electron donors. In this case introduction of electronegative substituents into the chelate ring is expected to inhibit the formation of OSCs of the type A and to enhance formation of complexes of type B. The introduction of fluorine-containing substituents into the chelate ring also creates additional steric hindrance for OSC formation. For A ligands the steric and inductive effects are additive, whereas for B ligands they act in opposite directions.

Moreover, considering the character of interactions between β-diketonates and outer-sphere ligands of groups A and B it is clear that acidic protons of A are usually less remote from the paramagnetic metal than protons of B.

To illustrate the influence of steric and induction factors on the stability of OSC, consider in more detail data [73] on the effect of substituents in Fe(III) β–diketonates on the stability of their OSCs with $CHCl_3$ and CH_3OH. As seen in Table 4, introduction of bulky substituents into the chelate rings of Fe(III) complexes leads to a significant decrease in the OSC stability constants with $CHCl_3$ in the above series of β–diketonates. This decrease seems to be primarily due to the steric effect.

Because of steric hindrance created by phenyl groups, molecules of $CHCl_3$ do not produce hydrogen bonds with oxygen atoms of the bis-*N*-phenylsalicylaldiminate of Cu(II) (Cu(N–Ph–Salim)$_2$). At the same time, such bonds are formed between $CHCl_3$ and Cu(N–Ph–Salim)$_2$py, in which oxygen atoms are less shielded by phenyl groups owing to the changes in the chelate structure caused by addition of the molecule of pyridine to the copper atom [74].

The variation of stability constants for OSCs with CH_3OH is somewhat less than for OSCs with $CHCl_3$ in a similar series of β–diketonates (compare the data of Table 4 for OSCs of $CHCl_3$ and CH_3OH with Fe(acac)$_3$ and Fe(pta)$_3$). This can be explained by a smaller steric hindrance for CH_3OH as compared to more bulky molecules of $CHCl_3$. Using the values of $\beta^{(H)}$ obtained for CH_3OH, it is possible to estimate the Taft coefficients, ρ^* and S [109] for equation

$$\log\left[\beta^{(H)}/\beta_0^{(H)}\right] = \rho^*\sigma^* - SE_s \tag{32}$$

where σ^* and E_s are respectively inductive and steric Taft constants for substituents in Fe(III) β-diketonates. The Taft coefficients [73] were $\rho^* = 0.4 \pm 0.2$ and $S = -0.1 \pm 0.1$, which indeed indicate a predominant inductive effect on the stability of OSCs with CH_3OH.

An electrostatic dipole–dipole interaction of outer-sphere ligands with metal complexes seems to be of minor importance in the case of β-diketonates. This is suggested by the absence of any correlation between the direction of the dipole moment of the molecule L and the direction of its outer-sphere coordination. For example, the molecules of chloroform and dichloromethane are bound with the positive dipole being oriented toward the metal complex [28], whereas for the molecules of toluene it is the benzene ring rather than the positively charged methyl group that is more close to the paramagnetic metal atom [25]. Moreover, $\beta^{(H)}$ for toluene is nearly the same as $\beta^{(H)}$ for benzene, which has no dipole moment at all [25].

It should be noted that the same outer-sphere ligand can form with the same metal complex OSCs of various structures due to interactions of different nature. Alkyl halides are examples of such ligands. At high concentrations, molecules of $CHCl_3$ and CH_2Cl_2 can be located in OSCs with Co(acac)$_2$py$_2$ both near the equatorial plane being bound via formation of hydrogen bonds and near the Z axis most probably, being bound via interaction with the π-system of coordinated pyridine [32].

As shown in section B.(iii), alkyl halides form complexes with coordinatively saturated tris- β-diketonates not only via formation of hydrogen bonds but also via some other routes. Consider this problem in more detail.

Considerable chemical shifts for ^{13}C atoms of alkyl halides with different paramagnetic complexes of transition metals, including Cr(acac)$_3$ and

$Fe(acac)_3$, have been observed [36–38]. No such effect was observed for analogous diamagnetic compounds. Thus the observed shifts can be attributed to the paramagnetism of the metal complexes. Shifts in ^{13}C NMR signals of some organic compounds in the presence of $Cr(acac)_3$ were also observed [89,110].

The magnetic anisotropy of $Cr(acac)_3$ and $Fe(acac)_3$ is known to be small [87], so that the pseudo-contact shift (see formula (31)) of the nuclei of outer-sphere ligands must also be quite small [35]. Therefore, the large (up to 100 ppm [38]) shifts of ^{13}C nuclei of alkyl halides seem to result from the contact interaction, i.e. from spin density delocalization onto the nuclei of outer-sphere ligands. A larger shift of ^{13}C nuclei compared to that of protons for $CHCl_3$ and CH_2Cl_2 seems to indicate [36–38] that these molecules are oriented in the OSC with their chlorine atoms toward the paramagnetic centre of the metal complex.

The fact that for alkyl halides the chemical shifts of ^{13}C nuclei exceed those for protons and at the same time the relaxation rates, $R_1^{(M)}$, for protons exceed those for ^{13}C nuclei (see Table 8) can be explained if we assume that alkyl halides form OSCs of two types with transition metal β-diketonates (i) via formation of hydrogen bonds and (ii) via interaction of halide atoms with metal complexes. As shown in section B.(iii), complexes of the first type are more stable ($\beta^{(H)} > \beta^{(C)}$). Therefore, coordination via hydrogen bonds is predominant and it is this coordination which is manifest in the concentration dependence of the parameter R_1 determined only by magnetic dipole–dipole interaction. The formation of this type of complex also determines variations in the solubility of the metal complexes at moderate concentrations of alkyl halides. However, with this coordination, there seems to be no marked delocalization of spin density onto carbon atoms of outer-sphere ligands, which eventually leads to the absence of the ^{13}C nuclei shifts. Complexes of the second type are less stable and therefore there can be few ligand molecules oriented in such a way, at least at low concentrations of alkyl halides. However, in this case a noticeable delocalization of spin density onto the outer-sphere ligand occurs and therefore complexes of the second type, rather than of the first, are detected in measurements of the ^{13}C nuclei shifts.

Thus, the model proposed for independent formation of various types of OSCs allows one to explain different trends in variations of the relaxation rates and of the chemical shifts for protons and ^{13}C nuclei of alkyl halides in the presence of $Cr(acac)_3$ and $Fe(acac)_3$ ($R_1^{(M)}(^1H) > (\gamma_H/\gamma_C)^2 R_1^{(M)}(^{13}C)$, but $\delta^{(M)}(^{13}C) > \delta^{(M)}(^1H)$). Moreover, this model illustrates once again a high sensitivity of some of the NMR spectroscopic parameters even to small admixtures of OSCs with coordination type other than the predominant one.

Examples are known when rather strong Lewis bases are displaced from the inner coordination sphere of metals upon addition of alkyl halides to the solution. A possible explanation for this phenomenon is the formation of an OSC. For example, at high concentrations of $CHCl_3$ in toluene solution, pyridine is partly displaced from the adduct Cu(N–Ph–Salim)$_2$py [74]. This effect can be explained by the coordination of a $CHCl_3$ molecule somewhere near the axial position thus creating steric hindrance for pyridine coordination. It seems that such coordination can occur either via interaction of the Cl atom of the $CHCl_3$ molecule with the Cu(II) atom (inner-sphere coordination) or via the interaction of the same atom with the π-system of the chelate ligand (outer-sphere coordination).

(ii) Two-centre outer-sphere coordination

The formation of an OSC can result from independent interactions of a metal complex with various functional groups of outer-sphere ligands. Thus one might expect that some outer-sphere ligands can be bound to the metal complex in a two-centre way, i.e. through simultaneous formation of two different outer-sphere coordination bonds. Indeed, coordination of this type seems to have been detected for OSCs formed by trichloroethylene with Cr(acac)$_3$ [42,43].

Based on the existence of two independent coordination routes for $CHCl_3$ with β-diketonates (via atoms H and Cl), one might expect that trichloroethylene would also form OSCs of these two types with Cr(acac)$_3$. If so, the concentration dependences of the ^{13}C nuclei shifts and of the proton linewidths of trichloroethylene in the presence of Cr(acac)$_3$ are expected to be described by formula (9) with different stability constants, $\beta^{(H)}$ and $\beta^{(C)}$ which characterize respectively the coordination of trichloroethylene via a hydrogen atom and via a chlorine atom.

However, it is seen in Table 11 that in all solvents studied, including those containing $CHCl_3$, $\beta^{(C)} = \beta^{(H)}$. In principle, such a coincidence of stability constants for different types of coordination can be accidental. However, if molecules of trichloroethylene formed complexes with Cr(acac)$_3$ via H and via Cl atoms independently they would compete with $CHCl_3$ for the two different sites of the outer coordination sphere in different ways since for chloroform OSCs with Cr(acac)$_3$ made via H and Cl atoms have different stability constants $\beta^{(H)}$ and $\beta^{(C)}$ (see above). In this situation, in the presence of $CHCl_3$ no coincidence of $\beta^{(H)}$ with $\beta^{(C)}$ for trichloroethylene is expected. Nevertheless, as seen in Table 11, upon introducing various concentrations of $CHCl_3$ into the solution the equality between $\beta^{(H)}$ and $\beta^{(C)}$ for trichloroethylene is retained. This seems to indicate that trichloroethylene is, most likely, coordinated to Cr(acac)$_3$ via simultaneous formation of bonds with the participation of both H and Cl atoms.

TABLE 11

Stability constants for OSCs of trichloroethylene with $Cr(acac)_3$ in various solvents ($T = 298$ K)

Solvent	$\beta^{(H)}$ ($l\ mol^{-1}$)	$\beta^{(C)}$ ($l\ mol^{-1}$)
CCl_4	0.14 ± 0.01	0.13 ± 0.01
0.1 mol l^{-1} $CHCl_3$ in CCl_4	0.07 ± 0.01	0.05 ± 0.01
0.5 mol l^{-1} $CHCl_3$ in CCl_4	0.01 ± 0.01	0.01 ± 0.01
Cyclohexane	0.40 ± 0.05	0.36 ± 0.05

This conclusion is also confirmed by calculation of the geometrical parameters of the complex formed by trichloroethylene and $Cr(acac)_3$ from the rates of paramagnetic spin–lattice relaxation, $R_1^{(M)}$, of ^1H and ^{13}C nuclei of trichloroethylene in the coordination sphere of $Cr(acac)_3$. The distances between the Cr atom and proton and both C nuclei of the molecule of trichloroethylene are listed in Table 8. Using Cartesian coordinates, for which the zero point coincides with the position of the C atom of the CHCl group of trichloroethylene, the axis X is directed along the CH bond and the axis Y is on the plane of the molecule of trichloroethylene; the Cr atom of the $Cr(acac)_3$ complex has the coordinates, $X = 2.7$ Å, $Y = 0.50$ Å, $Z = 2.8$ Å, the distance between the chlorine atom of the CHCl group and the Cr atom being 4.6 Å. These geometrical parameters agree with models of trichloroethylene coordination with $Cr(acac)_3$ illustrated in Fig. 7b. Note also from the experimental data on $R_1^{(M)}$ one cannot distinguish which centre of the $Cr(acac)_3$ complex Cr(III) atom (model I in Fig. 7b) or π-system of the neighbouring inner-sphere chelate ligand (model II in Fig. 7b) forms the bond with a chlorine atom of the trichloroethylene molecule. The distances between the trichloroethylene atoms and Cr(III) atom, which can be estimated for each of the above possibilities using molecular models, both fit the experimental data well. Conceivably both these types of coordination are present.

The paramagnetic shifts of organic molecules in the outer coordination sphere of $Cr(acac)_3$ are known to result from the Fermi-contact interaction. Therefore, the shifts of various nuclei provide information about delocalization of the spin density onto the molecular orbitals of the outer-sphere ligand. The largest shift (-30 ppm) is observed for the carbon atom of the CHCl-group of trichloroethylene. The shifts of the proton and of the second carbon atom are far smaller: 1.3 and -5.7 ppm, respectively. These paramagnetic shift values are in agreement with the proposed models of trichloroethylene coordination with $Cr(acac)_3$ if one assumes that the spin

TABLE 12

Paramagnetic shifts (ppm) of carbon nuclei and of oxygen of alcohols in OSCs with $Cr(acac)_3$ in CCl_4 solution ($T = 300$ K)

	^{17}O	$^{13}C_1$	$^{13}C_2$	$^{13}C_3$	$^{13}C_4$
Methanol	-38 ± 4	-6.9 ± 0.5			
Ethanol	-28 ± 2	-3.1 ± 0.2	-3.0 ± 0.2		
Isopropanol	-21 ± 1	-0.7 ± 0.1	-2.0 ± 0.1		
n-Butanol	-18 ± 2	-2.4 ± 0.2	-1.4 ± 0.1	-0.8 ± 0.1	-0.6 ± 0.1
t-Butanol	-12 ± 2	$+0.5 \pm 0.1$	-1.2 ± 0.1		

density is transferred onto the atoms of trichloroethylene through the coordination bond of the Cl atom.

Despite the two-centre type of coordination, the life time of the trichloroethylene–$Cr(acac)_3$ complex is rather short (see Table 6), indicating that the bonds responsible for its formation are rather weak.

We now proceed to the data on the outer-sphere coordination of various alcohols with $Cr(acac)_3$ complexes [47]. It is seen in Table 12 that the ^{13}C nuclei paramagnetic shifts of the alcohols studied are considerably smaller than for the oxygen nucleus. Such a distribution of paramagnetic shift agrees with the assumption of alcohol coordination via the oxygen atom. For all alcohols $\beta^{(C)} = \beta^{(H)}$ (see Tables 4 and 5). This is evidence for both the hydrogen atom and oxygen atom of the alcohol hydroxyl group being involved simultaneously in the formation of the bond with $Cr(acac)_3$. Likewise for trichloroethylene, it is impossible to determine reliably which centre of $Cr(acac)_3$ (Cr(III) atom or π-system of the neighbouring chelate cycle) forms the bond with the alcohol oxygen atom. Estimation based on molecular models suggests that bonding with the π-system is more preferred. However, it is not excluded that both coordination modes are present.

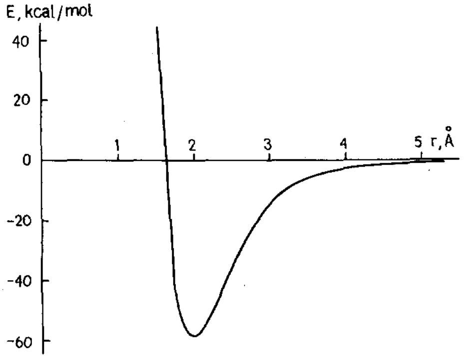


Fig. 8. Morse potential for the Cr–O bond.

It may seem at first glance that the distances between the atom of Cr(III) and those of Cl or O of trichloroethylene and alcohols are too large (from 4.5 to 5 Å) for the coordination bond to be formed directly between these atoms. However, simple estimates using a Morse potential with the dissociation energy $D_e = 60$ kcal mol^{-1}, equilibrium interatomic distance, $r_e = 2$ Å, and stretching frequency $\lambda = 460$ cm^{-1}, which are the values typical for the inner-sphere oxygen-to-metal coordination bonds, show (see Fig. 8) that for distances of 4–5 Å the energy of the direct interaction of the ligand atom with the metal atom is still about 2–3 kcal mol^{-1}. This value is close to the typical enthalpies of OSC formation.

(iii) Spin density transfer onto the outer-sphere ligands

Formation of outer-sphere coordinate bonds is often accompanied by the transfer (delocalization) of spin density onto atoms of outer-sphere ligands. The data discussed in the sections above allow us to draw some conclusions about possible mechanisms for this phenomenon.

The first work, in which the paramagnetic shifts of the solvent ($CHCl_3$) protons in the presence of complexes $[MI_3PPh_3]^-NBu_4^+$ (where M = Co(II), Ni(II)) were observed, seems to be that by Rettig and Drago [34]. The existence of paramagnetic shifts was accounted for by the formation of partly covalent hydrogen bonds I...H. Later paramagnetic shifts of protons of $CHCl_3$, CH_2Cl_2 [35] and CH_3OH [24] were discovered for solutions containing $Cr(acac)_3$. As in [34], the shifts were attributed to partial covalency of the outer-sphere bonds formed [25,35].

In the past years the spectrum of systems characterized by paramagnetic shifts of nuclei of outer-sphere ligands has been considerably broadened. For example, the paramagnetic shifts of ^{13}C and ^{15}N nuclei were detected for various organic molecules in the presence of various magnetically isotropic metal complexes having saturated inner coordination spheres (e.g. $Fe(acac)_3$ and $Cr(acac)_3$) [38,41–47,89,110–112].

Systematic studies of the paramagnetic shifts observed in alkyl halides upon coordination with paramagnetic transition metal complexes have been carried out in [36–41]. Paramagnetic shifts of ^1H and ^{13}C nuclei have been observed for alkyl halides of the type $CH_{4-n}X_n$ ($n = 1, 2, 3$; X = Cl, Br, I) through their outer-sphere coordination to complexes of the type MX_nL_{m-n} (M = Co(II), Ni(II); X = Cl, Br, I, NO_3; L = pyrazole, triphenylphosphine, pyridine; $m = 4, 6$; $n = 2, 3$) [36,37,39–41], as well as $Cr(acac)_3$ and $Fe(acac)_3$ [38]. In every case the paramagnetic shift of the ^{13}C nucleus considerably exceeds that of the proton of the alkyl halide. It has been proposed [36,37] that for complexes MX_nL_{m-n} the spin density is transferred onto carbon and hydrogen nuclei via the inner-sphere coordinate bond formed between the metal atom and the halogen atom of an organic molecule. This implies the formation of inner-sphere complexes with coordination numbers 5 and 7. However, doubts have later been expressed concerning the inner-sphere coordination of alkyl halides [38,39]. As an alternative explanation of the experimental data [36,37,39] a model of coordination which involved a donor–acceptor interaction between the pair of halogen atoms, one of which belongs to the metal complex and the other to the alkyl halide, has been proposed. At the same time, it has been mentioned [39] that such a model also does not take into account all the possible routes of spin density transfer onto the outer-sphere ligand molecules.

Thus, spin density is transferred from MX_nL_{m-n} to the alkyl halides via the coordinate bond produced by the halogen atom of these molecules. The coordination site of the metal complex at present is not certain. It could either be the metal atom or the halogen ligand in the inner sphere. For $Cr(acac)_3$ and $Fe(acac)_3$ the most probable mechanisms for spin density delocalization seem to be a weak direct interaction between the metal atom and a halogen atom of an alkyl halide at a long distance (see above) or an interaction of a halogen atom with the π-system of the chelate rings.

The situation with respect to the mechanism of spin density transfer onto alcohols coordinated in the outer sphere of β–diketonates is approximately the same as that for alkyl halides. The spin density seems to be transferred onto the alcohol molecules via the coordinate bond formed by the oxygen atom. A partner from the side of the metal complex is less clear. It also could be either the metal atom or the π-system of the chelate ligand.

For aromatic molecules, the most probable route of OSC formation is the interaction of the π-system of the aromatic ring with that of the chelate (see above). Therefore, it might be anticipated that spin density transfer from β-diketonates onto aromatic molecules would also occur via π–π interaction. However, the observed paramagnetic shift distribution over various atoms of the aromatic ring does not correspond to that expected for "pure" π–π mechanism of spin density delocalization [44].

For example, for this latter mechanism, the shifts $\delta^{(C)}$ and $\delta^{(H)}$ have opposite signs and the condition $|\delta^{(H)}| > |\delta^{(C)}|$ is typical [113–115]. On the contrary, for benzene (see Table 10) $\delta^{(C)}$ and $\delta^{(H)}$ induced upon outer-sphere coordination have the same signs, $\delta^{(H)}$ being less than $\delta^{(C)}$ by one order of magnitude. At present one can scarcely make any reliable conclusions about the nature of this effect. Some more evidence is necessary to clarify this problem. We can state only that there seem to be more than one channel of spin density transfer to the aromatic outer-sphere ligands and the distribution of chemical shifts observed reflects the superposition of several delocalization mechanisms whose contributions are comparable.

It follows from the results discussed in this section that the spin density transfer (though quite small) onto outer-sphere ligands is typical for almost all types of OSCs studied. This fact indicates a partially covalent (although to a very low extent) character of donor-acceptor bonds responsible for the formation of OSCs.

F. EFFECT OF OUTER-SPHERE COORDINATION ON THE STRUCTURE OF METAL COMPLEXES

The total interaction energy of outer-sphere ligands with the metal complex (6–15 kcal mol^{-1}, see section B) is high enough to perturb noticeably its geometric and electronic structure in solution. It might be anticipated that the scale of these perturbations would be commensurate with that of perturbations caused by packing effects in crystals.

Substantial changes in proton paramagnetic shifts of inner-sphere ligands (acetylacetonate-ion (acac) and bases B) for complexes of $\text{Co(acac)}_2\text{B}_2$ (where B stands for pyridine, piperidine or their derivatives) have been observed upon formation of OSCs with $CHCl_3$ and CH_2Cl_2 [30]. The magnetic anisotropy parameter P and the length D of the Co–N coordination bond (see Table 13) have been calculated from the shifts of *ortho-*, *meta-* and *para*-protons of B [30,56]. It is seen in Table 13 that the parameter P increases as the strength of the Lewis base B increases. The parameter P for Co(II) complexes is known to be determined by the zero field splitting [31]. This splitting usually increases as the field of ligands becomes less symmetric. One can, therefore, suppose that an increase in parameter P in $CHCl_3$ and CH_2Cl_2 solutions as compared to that in C_6H_{12} solution reflects a decrease in the symmetry of the ligand field around the Co(II) atom upon coordination of $CHCl_3$ and CH_2Cl_2 molecules to the outer sphere of $\text{Co(acac)}_2\text{B}_2$.

TABLE 13

Paramagnetic shifts [a] $\delta^{(M)}$ of protons, length D of the Co–N bond and parameter of magnetic anisotropy P of $\text{Co(acac)}_2\text{B}_2$ complexes

B	Solvent	$\delta^{(M)}$ (ppm) [a]					$10^3 \cdot P$ (Å)^3	$D \pm 0.10$ (Å)
		CH	CH_3	*o*-H	*m*-H	*p*-H		
py	C_6H_{12}	−17.4	−24.2	−44.0	−2.9	15.4	2.55	2.22
	CCl_4	−21.2	−24.7	−46.0	−2.5	18.4	2.85	2.26
	$CHCl_3$ or CH_2Cl_2	−23.6	−25.7	−43.0	−0.6	22.8	4.10	2.40
pipe	C_6H_{12}	−33.0	−27.6	34.0	18.0	25.5	3.74	2.60
	C_6H_6	−32.2	−27.6	33.5	21.6	29.1	4.19	2.50
	$CHCl_3$ or CH_2Cl_2	−26.0	−25.3	35.0	22.6	28.3	4.69	2.40

[a] The minus sign (−) denotes a shift towards low field.

This agrees with the data concerning the influence of outer-sphere coordination on the zero field splitting for the magnetic sub-levels of the Fe(acac)$_3$ complex. From analysis of frequency dependences of $R_1^{(M)}$ for CH$_3$-protons the zero field splitting for Fe(acac)$_3$ has been found [57,58]. This splitting changes upon formation of OSCs, becoming larger the more stable are the OSCs (see Table 14).

As is seen in Table 13, outer-sphere coordination can significantly affect the length (D) of the coordinate bond between the metal atom and nitrogen atom of B. It is interesting that the variations in D are opposite for Co(acac)$_2$ adducts with py and pipe: formation of rather stable OSCs with CHCl$_3$ and CH$_2$Cl$_2$ leads to an increase of D for py and to a decrease of D for pipe. The nature of this phenomenon is not yet clear. Note also that the value of D measured by NMR for Co(acac)$_2$py$_2$ in cyclohexane, which is inert toward outer-sphere coordination is 2.2 ± 0.1 Å, i.e. is close to the value found from X-ray data for the crystal of the same complex (2.2 Å [117]).

For metal complexes the difference in energy of different isomers is often rather low. There are many examples which show that the change in the solvent composition noticeably shifts the equilibrium for transitions between these isomers. The ratio of the concentrations of the tetrahedral and planar isomers of bis-(N-isopropyl-salicylaldiminate) of Ni(II) increases [62] as the capability of the solvent molecules to form outer-sphere complexes via hydrogen bonds increases. This effect can be accounted for in that for the square-planar isomer the approach of outer-sphere ligands to the oxygen atoms is sterically hindered because of the large volume of the nitrogen atom substituent of the inner-sphere chelate ligand, whereas in a tetrahedral isomer, oxygen atoms are more accessible and can form hydrogen bonds with solvent molecules.

The dependence of isomeric composition on the solvent composition has also been observed for [(η^1-allyl)Pt(PPh$_3$)(2,6-Me$_2$C$_6$H$_3$NC)Cl]. At low temperature only the η^1-allyl isomer exists in toluene solution, whereas various isomers of this complex exist in CH$_2$Cl$_2$ solution [118].

TABLE 14

Zero field splitting Δ for Fe(acac)$_3$ in different solvents [43,44]

Solvent	Δ (cm^{-1})
CCl$_4$	0.9
6.3 mol l^{-1} CD$_3$CN in CCl$_4$	1.3
CDCl$_3$	1.5 ± 0.2
4.0 mol l^{-1} CD$_3$OD in CCl$_4$	1.7
Crystal [116]	0.11 ± 0.01

The influence of the solvent on the ratio between Δ and λ forms of geometrical isomers of transition metal chelates with optically active ligands is also well known (see [119–121] and refs. therein).

Some examples are also available concerning the influence of outer-sphere interactions on the equilibrium between spin isomers of metal complexes. In toluene solutions, Fe(III) porphyrins are predominantly in a high-spin state, whereas in $CHCl_3$ and CH_2Cl_2 solutions a considerable proportion of these compounds is in a low-spin state [61]. The influence of the formation of outer-sphere complexes on the equilibrium between the isomers of Fe(II) complexes has been studied in detail both in solutions and in crystals [59,60,122]. Addition of alcohol molecules to the outer sphere often induces a transition of Fe(II) complexes from the low- to high-spin state. In this case, the stability of high-spin isomers increases as the strength of the hydrogen bond between the inner-sphere ligands and alcohol molecules increases. Thus, addition of alcohol molecules to the outer sphere seems to weaken the coordinate bonds of inner-sphere ligands with metals, which leads to the transition from low-spin to high-spin complexes. This conclusion is supported by X-ray data indicating an 0.2 Å increase of the length of these coordination bonds upon formation of OSCs [60].

Stabilization of various forms of the complex owing to outer-sphere coordination of the solvent molecules can also affect the equilibrium of addition of inner-sphere ligands to the metal complex. For example, $CHCl_3$ was found to bind more strongly to $CoCl_2py_4$ than to $CoCl_2py_2$ [123]. This provides the shift in the equilibrium $CoCl_2py_2 + 2py \rightleftharpoons CoCl_2py_4$ toward $CoCl_2py_4$ upon addition of $CHCl_3$. The observed changes in the equilibrium constants can be quite significant. For example, substitution of the $CHCl_3$ solvent by toluene leads to nearly the same changes in the stability constants for an axial ligand coordination to Cu(II) and Co(II) porphyrins as does the change of an axial ligand (pyridine or piperidine) [124].

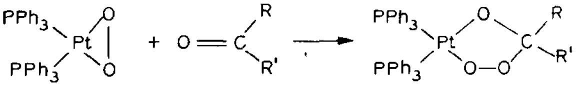
Thus, the formation of outer-sphere complexes can result in quite substantial rearrangements of the inner coordination sphere of metal complexes.

G. INFLUENCE OF OUTER-SPHERE COORDINATION ON THE CHEMICAL PROPERTIES OF METAL COMPLEXES

The nature and properties of OSCs presented in the previous sections allow one to draw some conclusions about the expected influence of outer-sphere coordination on chemical and, in particular, on catalytic properties of electrically neutral metal complexes.

Formation of an OSC can weaken coordinate bonds of inner-sphere ligands with metal atoms. It should therefore be anticipated that reactions in which the rupture of chemical bonds between inner-sphere ligands and the metal atom is the rate-determining step will be accelerated by outer-sphere coordination of solvent molecules. For reactions of such a type the activation energy has to decrease by an extent close to the energy of outer-sphere coordination, i.e. by 2–5 kcal mol^{-1}. At room temperature this corresponds to an increase of reaction rate by several tens to several hundred times.

The validity of this idea can be supported by a series of examples. For example insertion [125] of ketones into the metal–oxygen bond in adducts of metal complexes with molecular oxygen is accelerated by methanol. This



acceleration has been explained by the weakening of the Pt–O bond, into which ketones are inserted, upon formation of the OSC with alcohol. An analogous explanation has also been suggested for the catalytic action of proton-donor molecules [126,127] and organo tin compounds [128] in reactions of ligand substitution in the inner coordination sphere.

Ligand substitution processes represent an important step in many catalytic reactions involving metal complexes. Therefore the possibility of acceleration of these processes through OSC formation is of interest for catalysis by metal complexes.

Orientation of reagents in the outer coordination sphere of metal complexes promoting their interaction with each other might be a possible mechanism for the catalytic action of metal complexes in some reactions. In this case, the gain in the activation entropy must be close to the change of the entropy upon outer-sphere coordination, i.e. ca. 5–15 e.u. At room temperature this aids acceleration of the reaction from ten to one hundred times.

An example of a catalytic process for which the orientation effect of the above type seems to be important is the formation of urethanes in the coordination sphere of $Fe(acac)_3$ [67]. According to [67], the role of the catalyst in this process consists of the creation of favourable conditions for the formation of a co-planar complex between the reagents in which an optimal mutual orientation of isocyanide and alcohol, providing a noticeable decrease in the activation energy, is accomplished.

Apparently, reagents can be oriented most efficiently owing to the combined action of different types of outer-sphere coordination. For example, in the ligand substitution reaction between Fe(III) tris-benzoylacetonate and acetylacetone the catalytic action of alcohols has been explained by protonation of the emerging ligand and formation of Fe(III) alcoholates [129]. There are reasons [129] for suggesting that this process is preceded by the two-centre coordination of alcohol with a Fe(III) complex by means of formation of the hydrogen bond between the alcohol and the oxygen atom of the inner-sphere chelate ligand. There is also a weak direct coordinate bond (with a large interatomic distance) between the oxygen atom of an alcohol and the Fe(III) atom. It is possible that with such coordination both the necessary orientation of an alcohol near the metal complex and the conditions for weakening of the inner-sphere coordination bond between the metal atom and oxygen atom of the chelate ligand can be accomplished.

Outer-sphere coordination can also be important for reactions in which proton transfer is the rate-determining step. The molecules of solvents such as alcohols and amines coordinated in the outer sphere can retain the capability to form hydrogen bonds with other molecules of the medium. In this case, the transfer of a proton or of a hydrogen atom from one reagent to another in the coordination sphere can occur via the system of outer-sphere hydrogen bonds. Based on this model, the catalytic action of alcohols in the formation of Schiff bases in the coordination spheres of Cu(II), Ni(II) and Zn(II) [130] and of semiacetals in the coordination sphere of Fe(III) [131] has been explained.

The formation of outer-sphere complexes between reagents and oxygen molecules involved in the inner coordination sphere can also be important for heterogeneous reactions catalyzed by metal oxides. In this connection note the results of ref. 132 which seem to indicate an important role for the interaction between hydrogen atoms of the reagents and oxygen atoms of the catalysts in oxidative reactions of hydrocarbons proceeding via activation of C–H bonds. One could expect that a preliminary outer-sphere coordination of hydrocarbons bringing in contact the atoms interacting at the rate-determining step accelerates such catalytic reaction.

Note also that the outer-sphere coordination of reagents appears to be essential for biochemical reactions catalyzed by metal-containing enzymes. The principle of acceleration of chemical transformations by preliminary favourable orientation of reagents by virtue of molecular forces of the hydrogen bond type or hydrophobic interactions is widely involved in enzymatic catalysis [133].

Thus, the outer-sphere coordination of reagents and the medium by metal complexes in solution, on solid surfaces and in enzymes is indeed expected to affect noticeably catalytic reactions.

One can suggest that the outer-sphere coordination of organic molecules by metal complexes can also be important for such processes as extraction of metals by chelates [134] and adsorption chromatography of metal complexes [135,136]. Indeed, when used as an organic phase, solvents capable of producing stable OSCs are expected to provide more complete extraction of chelates from the water phase. When separating metal chelates by the adsorption chromatography method the intermolecular interactions of these chelates with the functional groups of adsorbents are very important. These interactions seem to have the same nature as those responsible for the formation of OSCs in solutions. For example, adsorption of tris-β-diketonates on supports containing hydroxyl groups is likely to occur via formation of hydrogen bonds between these hydroxyl groups and the oxygen atoms of β-diketonates. In this situation, one might expect a certain correlation between the efficiency of chromatographic separation of chelates and their capability to produce OSCs in solutions via formation of hydrogen bonds.

H. CONCLUSIONS

It follows from the data presented in this review article that solvation of electrically neutral metal complexes with organic solvents has a discrete character and consists of the formation of outer-sphere complexes (OSCs) of a specific composition and structure. Fairly weak intermolecular interactions between the outer- and inner-sphere ligands, such as formation of hydrogen bonds, donor–acceptor interactions involving π-systems, electrostatic interactions of molecular dipoles of the medium with non-compensated charges of inner-sphere ligand atoms, as well as weak direct interactions between outer-sphere ligands and metal atoms at large distances, are responsible for OSC formation.

The formation reactions of outer-sphere complexes occur in a stepwise manner. The typical OSC stability constants at room temperature are within the range 0.1–10 l mol^{-1}. The typical enthalpies and entropies of addition of an outer-sphere ligand are $\Delta H^0 = -(2\text{–}5)$ kcal mol^{-1} and $\Delta S^0 = -(5\text{–}15)$ e.u. However, since customarily several molecules of solvent are added to the outer sphere, the total change in the enthalpy and entropy during the course of OSC formation is usually several times higher than the values given and can be commensurate with the enthalpy of addition of the axial inner-sphere ligands to transition metal bis-chelates.

The molecular life times in the outer sphere ($\tau_h \simeq 10^{-10}$ s) are nearly the same as the characteristic life times of diffusion pairs in liquids. However, there is a principal difference between diffusion pairs and OSCs. In diffusion pairs the collided molecules are oriented randomly, whereas in OSCs the ligands are oriented in a definite order which is thermodynamically most favourable. The loss in entropy resulting from orientation is compensated by the gain in enthalpy achieved by OSC formation.

Addition of molecules to the outer sphere can appreciably perturb the electronic and geometric structure of metal complexes. For example it can lead to the transition from low- to high-spin state of a complex, change the lengths of chemical bonds between a metal atom and inner-sphere ligands, and also modify the symmetry of the inner coordination sphere (from square-planar to tetrahedral, for example).

As a result, the formation of outer-sphere complexes can change considerably the physico-chemical properties of metal complexes, such as their solubility. Also OSC formation seems to noticeably affect the rate of chemical transformations such as substitution reactions of inner-sphere ligands, insertion of molecules into a metal–ligand bond and transfer of a hydrogen atom between different functional groups of inner-sphere ligands. In some cases, orientation of reagents in the outer sphere is likely to promote catalytic transformations assisted by metal complexes.

Thus the formation of outer-sphere complexes seems to have a marked effect upon the structure and the physico-chemical properties of metal complexes in solution.

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