
STUDY OF THE NATURE OF THE CHEMICAL BOND IN THE OUTER-SPHERE ADDUCTS OF ELECTRICALLY NEUTRAL COMPLEXES AND ORGANIC MOLECULES

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Outer-sphere complex formation by various organic molecules with the β-diketonato compounds of transition metals have been studied by NMR. The effective stability constants of the complexes and the effective spin-lattice relaxation times of the protons of the ligands have been measured. It has been concluded that there are two types of coordination of the outer-sphere ligands: that due to hydrogen bonding with the oxygen atoms of the chelate compounds, and that due to interaction with the π-system of these chelate compounds.

The physicochemical properties of the complexes of transition metals in a liquid depend on the outer-sphere coordination of the molecules of the medium. For charged metal-containing complexes the nature of the interaction responsible for the outer-sphere coordination is for the most part clear (electrostatic ionic or ion–dipole interaction), but for neutral complexes there is no generally accepted viewpoint on this topic. In [1] it was shown that the most stable outer-sphere complexes (OSC) with the β-diketonato compounds of transition metals are formed by molecules capable of forming hydrogen bonds as acids. The outer-sphere coordination of organic molecules as a result of the formation of hydrogen bonds with the oxygen atoms of a chelate compound was confirmed in [2] by infrared spectroscopic data. On the other hand, it was concluded in [3] that the OSC formed by Co(III) pyrazolylborate and organic molecules involve dipole–dipole interaction. Subsequently, however, the authors of [3], in a study of the reaction with Cr(III) acetylacetonate, also concluded that hydrogen bonding is the decisive factor in the formation of outer-sphere adducts between neutral complexes and the molecules of the solution [4]. The existence of OSC formed by metal-containing complexes and molecules which do not exhibit proton-donor properties [1, 3], however, indicates that the outer-sphere interaction does not reduce merely to hydrogen bond formation.

In the present work, an attempt was made to investigate the nature and properties of the OSC formed by the β-diketonato complexes of transition metals with the solvent molecules fre-
quently used in organic chemistry: benzene, chloroform, acetone, etc. A particularly con-
venient method for studying the outer-sphere adducts formed by the molecules of a medium with
paramagnetic complexes is the NMR method, which is sensitive to even weak intermolecular in-
teractions and which makes it possible to reach conclusions regarding the relative orienta-
tion of the interacting species [5].

EXPERIMENTAL

The measurements were made on a Bruker SXP-4-100 pulse Fourier NMR spectrometer at a
temperature of 25 ± 2°C. The mathematical treatment of the results was carried out on the
BNC-12 computer forming part of the instrument. The spin-lattice relaxation time \( T_1 \) was
measured by inverting the magnetization by means of the usual pulse sequence \( (T - 180° - T - 90°) \) [6]. The experimental error in the determination of \( T_1 \) did not exceed 5%. The
solvents used were purified by standard methods [7]. ROSN grade Cr(III) acetylacetonate
Cr(AA)₃ was used without additional purification. Fe(AA)₃ and Cu(AA)₂ were subjected to vacu-
um sublimation at \( t = 110° \) immediately before the preparation of the solutions. Chromium-
(III) and iron(III) trifluoroacetylacetonates CrT₃ and FeT₃ and chromium(III) heptafluorodi-
methyloctanedionate Cr(FOD), were prepared in the chromatographic analysis group of the In-
stitute of Chemical Physics of the Academy of Sciences of the USSR, and used without further
purification. In all the experiments, the concentration of the metal-containing complexes
(0.001-0.1 M) was much lower than the concentration of the outer-sphere ligands being stud-
ied (0.05-1.5 M).

The rate of longitudinal relaxation of the nuclei of the molecules being studied in the
solution containing the paramagnetic metal-containing complexes can be represented as the
sum of three components:

\[
R_1 = \frac{1}{T_1} = R_{1M} + R_{1V} + R_{1d}.
\]  

The first term in Eq. (1) is due to outer-sphere complex formation and is determined by the
rapid relaxation of the nuclei in the second coordination sphere of the paramagnetic metals; it is known [5] that only the dipole interaction of the electronic and nuclear spins makes a
contribution to \( R_{1M} \).

The second term \( R_{1V} \) is due to the relaxation arising as a result of the dipole-dipole
interaction between the spin of the nucleus and the spins of the metal-containing complexes
in stochastic complexes (complexes formed by random collisions), and also the relaxation re-
sulting from interaction with the spins of complexes at a distance from the given nucleus.
The volume correction \( R_{1V} \) is readily taken into account. Thus a number of authors have noted
the absence of specific interaction between cyclohexane and the β-diketonato compounds of
transition metals [8-10]. We therefore estimated the volume correction for the rate of re-
laxation of the substances being studied from the rate of the paramagnetic relaxation of the
protons of cyclohexane, used as solvent, or added specially to the solutions as an internal
standard. It was assumed that the volume corrections for different substances are the same;
this is confirmed by the fact that the rates of the paramagnetic relaxation for cyclohexane
and another inert solvent, hexamethyldisiloxane (HMDS), coincide.

The third term in Eq. (1) is the diamagnetic relaxation rate and is equal to the rate
of relaxation of the nuclei in the solution being studied in the absence of paramagnetic
additives. Data on the proton relaxation of some of the outer-sphere ligands studied, giving
an idea of the scale of values of the corresponding contributions to the relaxation rate, are
summarized in Table 1.

Under the conditions of rapid exchange of the molecules being studied between solution
and the solvate layer of the metal-containing complexes under conditions of equilibrium be-
tween OSC of different composition

\[
M + nL \rightleftharpoons ML + (n - 1) L \rightleftharpoons \ldots \rightleftharpoons ML_n
\]  

with the condition \([M]_o/[L]_o << 1\), it is possible to write

\[
R_{1M}^e = \sum_{i=1}^{n} \frac{iR_{1i}^0 [ML_i]}{[L]_o}.
\]