JOURNAL OF CATALYSIS 39, 205–212 (1975)

Nuclear Magnetic Resonance Studies of Complexes Formed by Adsorbed Molecules and Tetrahedral Co^{2+} and Ni^{2+} Ions

V. B. KAZANSKY, V. YU. BOROVKOV AND G. M. ZHIDOMIROV

N. D. Zelinsky Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow, U.S.S.R.

Received July 23, 1973; revised October 30, 1974

The NMR technique was applied to the study of surface complexes of olefins and saturated hydrocarbons with Ni^{2+} and Co^{2+} ions on Aerosil and of molecular hydrogen with these ions in Y-zeolite. Heats of formation of complexes of saturated hydrocarbons with Co^{2+} were 2–2.5 kcal/mol, and those for molecular hydrogen complexes were about 4 kcal/mol. The structures of complexes formed with paramagnetic ions on the surface of Aerosil are discussed.

INTRODUCTION

It has already been reported that molecules physically adsorbed on silica gel and Aerosil do not show large broadening in their NMR spectra and can be studied by high resolution NMR (*1–4*). Varied line widths in the spectra indicate the interaction of certain groups of molecules with active centers of the surface. A study of proton resonance broadening of H_2O molecules as a function of silica gel surface coverage was reported by Bermudez (*5*). The data obtained were explained by a fast exchange of the protons of water molecules with surface hydroxyls. We also found (*6*) that, in the presence of transition metal ions with short relaxation times, on SiO_2 surfaces the NMR spectra of adsorbed molecules show in addition to the line broadening considerable paramagnetic shifts due to the formation of surface complexes involving these ions. The shifts were increased if the surface coverage was decreased. This can be explained by a fast exchange between coordinated and physically adsorbed molecules.

The present paper, which continues the latter investigation, concerns the study of the interaction of various molecules with bivalent cobalt and nickel ions on the Aerosil surface, and with ions introduced into NaY zeolite by ion exchange.

The adsorption of hydrogen, olefins, paraffins, benzene, cyclanes and cyclenes has been studied, and it was found that with these molecules labile surface complexes involving transition metal surface ions are formed.

EXPERIMENTAL METHODS

a. Preparation of Samples

The Aerosil was made by burning $SiCl_4$ in oxygen. Initially its surface area was 300 m^2/g. After washing with distilled water and calcination in air at 500°C, its surface area decreased to 200 m^2/g, but was then stable to repeated wetting and calcining. Nickel or cobalt ions were introduced by impregnation with aqueous solutions of the nitrates. After drying *in vacuo* at room temperature, the impregnated samples were heated for 2–3 hr *in vacuo*, in the absence of vacuum grease, at a residual pressure of 10^{-4} Torr (at 500°C

for cobalt and 650°C for nickel ions). The metal content was 0.5 wt%.

CoNaY and NiNaY zeolites were prepared by ion exchange with cobalt and nickel nitrates. The Co^{2+} content in CoNaY zeolite was 12–13 ions/unit cell, and that of Ni^{2+} in NiNaY zeolite was 6–7 ions/unit cell. The vacuum treatment was carried out at 450°C for 4 hr.

Approximately 0.5 g quantities of both Aerosil and zeolite samples were pretreated for each run. Glass ampoules with diameters of 9 mm were used. Consequently, the treatments were "deep bed" calcinations.

Optical uv diffusion reflectance spectra were obtained on a Unicam SP-700 spectrophotometer.

b. *Measurements of NMR Spectra of Adsorbed Molecules*

NMR spectra were measured on a USSR-made RS-60 spectrometer, with an operating frequency of 60 MHz. Proton stabilization of the magnetic field was used. To increase the sensitivity of the spectrometer the magnetic field was modulated with a frequency of 32 Hz. The spectra were recorded as the first derivatives of the absorption lines. Radio frequency scanning of the spectra allowed the study of NMR signals over a range of 30 kHz. The maximum resolution was about 0.5 ppm.

The glass ampoules containing the pretreated samples were placed in the spectrometer coil and joined to the vacuum unit through a vacuum break-seal (*7*). Then the system was thoroughly evacuated, the break-seal was broken, and the adsorption experiment was carried out. This technique allowed simultaneous measurements of adsorption and NMR spectra for the same sample in a temperature range of -100 to $+100$°C.

Before measurements, unsaturated hydrocarbons (ethylene, propylene, cyclohexene) and saturated ones (*n*-hexane, isopentane, cyclohexane, 1,4-*cis*- and *trans*-dimethylcyclohexane) were purified (to remove traces of oxygen) by the freeze–pump–thaw method. Molecular hydrogen was purified by diffusion through a glowing palladium capillary.

RESULTS

a. *Reflectance Spectra of the Samples*

The state of nickel and cobalt ions on the Aerosil surface was checked by uv diffusion reflectance spectroscopy. The spectra of the samples dried *in vacuo* at room temperature corresponded to octahedral coordination of both nickel and cobalt ions. After thermovacuum treatment at elevated temperatures, some new bands appeared and the lines from the octahedral ions became weaker. After treatment at 500°C for cobalt and 650°C for nickel the spectra were unaffected by a further temperature increase (Fig. 1).

An intense band at 14,000 cm^{-1} for bivalent cobalt ions indicates their tetrahedral or trigonal coordination. The spectra of Ni^{2+} ions also correspond to tetrahedral or trigonal coordination (an absorption band at 13,000–15,000 cm^{-1} that is usually

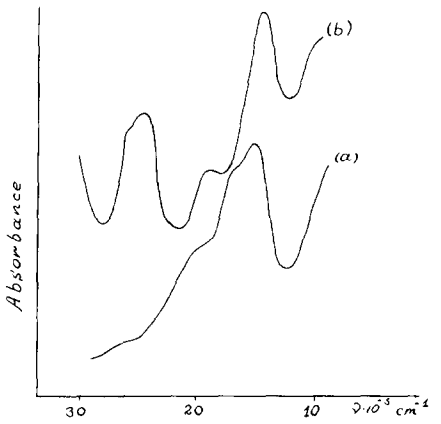

FIG. 1. Optical diffuse reflectance spectra of (a) Co^{2+} ions on Aerosil and (b) Ni^{2+} ions on Aerosil after vacuum treatment at high temperature.

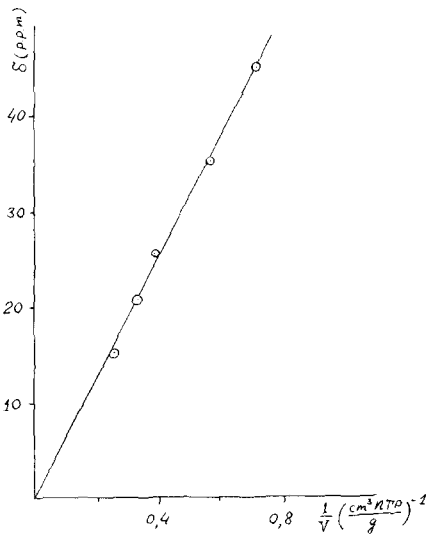

FIG. 2. Dependence of the NMR line shifts upon the amount adsorbed for ethylene on a Ni^{2+}-containing Aerosil. The spectra were recorded at −50°C.

ascribed to the $^3T_1(F)$–$^3T_1(P)$ transition). A more detailed study of Co^{2+} and Ni^{2+} ions supported on silica gel is given in Refs. (*8* and *9*).

The state of bivalent cobalt ions in CoNaY zeolite also corresponds either to tetrahedral or trigonal coordination depending on the pretreatment temperature (*10*). The published data on the state of bivalent nickel ions in zeolites are discussed in (*11*).

b. Adsorption of Unsaturated Hydrocarbons (Ethylene, Propylene, Cyclohexane)

The spectra of ethylene adsorbed at −50°C on Aerosil with Co^{2+} and Ni^{2+} ions show one line, shifted to higher fields compared to the spectrum of physically adsorbed molecules. Figure 2 shows the observed shifts as a function of the reciprocal of the amount of ethylene adsorption on a nickel sample.

Figure 3 shows the NMR spectra of propylene adsorbed on Aerosil with Co^{2+} ions at +10°C. They consist of two lines: one shifted to higher fields corresponds to α-protons at the double bond, and the other one slightly shifted to lower fields is due to the methyl group. With increasing pressure or surface coverage these two lines join together.

The spectrum of propylene adsorbed on a nickel sample is more complicated. It consists of four lines (Fig. 3). Three of which are shifted to higher fields correspond to the different protons at the double bond and the fourth one that is shifted to lower fields is caused by the methyl group. With a decrease in surface coverage the line widths and the shifts increase. Two central lines in spectra d, e and f (Fig. 3) are not resolved because of a

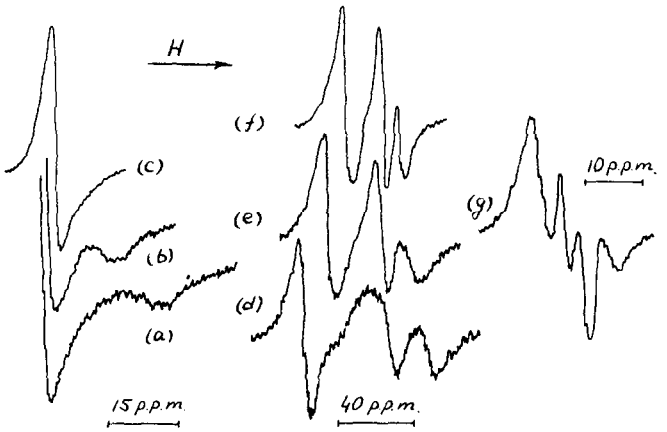

FIG. 3a,b, and c. NMR spectra of propylene adsorbed on a Co^{2+}-containing Aerosil at equilibrium pressures of 30, 60 and 180 Torr, respectively. (d,e,f, and g) NMR spectra of propylene adsorbed on a Ni^{2+}-containing Aerosil at equilibrium pressures of 3,6 and 15 and 150 Torr, respectively. All spectra were recorded at +10°C.

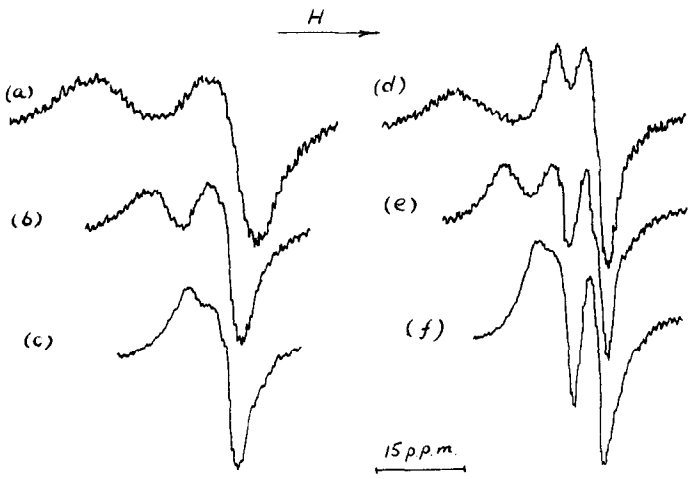

FIG. 4a, b, and c. NMR spectra of cyclohexene adsorbed on a Co^{2+}-containing Aerosil. Adsorbed amounts were 1.5, 3.5 and 9.0 cm^3 NTP/g, respectively. (d, e, and f) NMR spectra of cyclohexene adsorbed on a nickel sample. Adsorbed amounts were 5.5, 8 and 11 cm^3 NTP/g, respectively. The measurements were made at room temperature.

large magnetic field modulation necessary for adequate sensitivity at low surface coverage.

Figure 4 shows the NMR spectra of cyclohexene at various amounts of adsorption. Both for cobalt and for nickel samples they show one line caused by β-protons shifted to lower fields and another one caused by γ-protons. The position of the latter is almost independent of surface coverage. The line for α-protons is invisible presumably because of considerable broadening and a lower relative intensity.

In the spectra of cyclohexene adsorbed on a nickel sample, in addition to the lines from β- and γ-protons there is another narrow line shifted to lower fields. Its position is independent of surface coverage. As shown in Fig. 4 the lines from β- and γ-protons join together when the amount of C_6H_{10} adsorption increases.

c. *Adsorption of Saturated Hydrocarbons (n-Hexane, Isopentane, Cyclohexane, 1,4-cis and trans Dimethylcyclohexane)*

The NMR spectra of adsorbed saturated hydrocarbons recorded at room temperature showed only one symmetrical line. For the Aerosil samples containing Ni^{2+} ions, no considerable shifts were observed, whereas for cobalt samples the lines were strongly shifted to higher fields relative to those from physically adsorbed molecules.

Figure 5 shows these shifts versus the reciprocal of the amount adsorbed for dif-

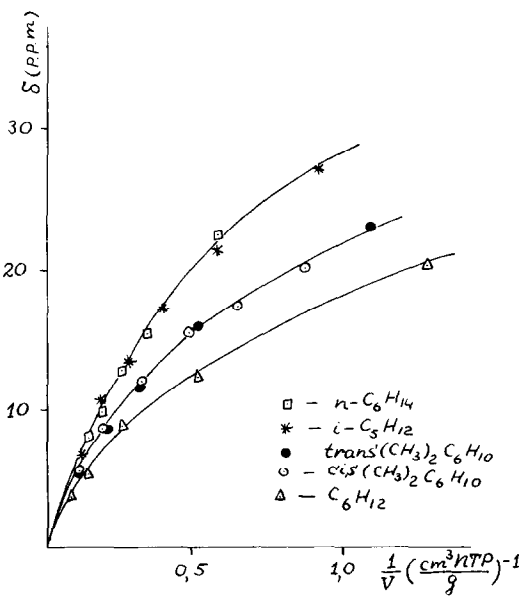

FIG. 5. Line shifts to higher fields as a function of the reciprocal of adsorbed amounts in the spectra of different saturated hydrocarbons adsorbed on Co^{2+} ions supported on Aerosil. The spectra were recorded at room temperature.

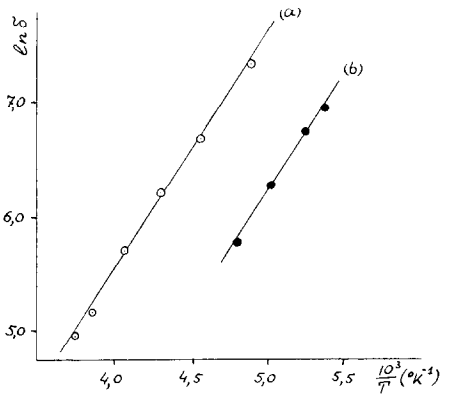

FIG. 6. Line shifts to lower fields (Hz) as a logarithmic function of the inverse absolute temperature in NMR spectra of adsorbed hydrogen on (a) CoNaY zeolite, (b) NiNaY zeolite.

ferent hydrocarbons at room temperature. For *n*-hexane the experiments were also carried out at higher temperatures. The shifts decreased when the temperature was increased.

d. Adsorption of Molecular Hydrogen

Hydrogen adsorption on zeolites was studied in a wide temperature range at a constant hydrogen pressure of 700 Torr. The position of the H_2 line was temperature independent for CoNaY zeolite above 273°K and for NiNaY zeolite above 215°K. Below these limits a shift to lower fields became noticeable, exponentially increasing with lowering temperature (Fig. 6).

DISCUSSION

Earlier (*6,12*) we showed that large paramagnetic shifts in the NMR spectra of adsorbed molecules and their strong dependence on surface coverage are due to the formation of complexes involving surface transition metal ions. The observed shifts, δ, of the lines in the spectra relative to those for physically adsorbed molecules, if a fast exchange between the complexes and physically adsorbed molecules takes place, are described by the expression (*12,13*):

$$\delta = N_c \cdot \delta_c, \qquad (1)$$

where N_c is the mole fraction of the complexed molecules; δ_c is the line shift of the complexed molecules.

The amount of surface complexes is determined by the equilibrium:

$$M + A_{ads} \overset{K_c}{\rightleftarrows} [MA]. \qquad (2)$$

In this case $$N_c = \frac{K_c \cdot n}{1 + K_c V}, \qquad (3)$$

where n the total number of active centers involved in complex formation,

V the total number of adsorbed molecules.

Consequently

$$\delta = \frac{K_c \cdot n\delta_c}{1 + K_c V}. \qquad (4)$$

This expression was deduced on the basis of an assumption that only single molecules are involved in the coordination sphere and the number of the surface complexes is much less than the total number of adsorbed molecules.

Two extreme cases should be discussed:

(a) $K_c V \gg 1$; $$\delta = \frac{n}{V}\delta_c. \qquad (5)$$

This corresponds to the formation of "stable" complexes. All of the active centers are occupied. There should be a linear inverse dependence of the line shifts in the NMR spectra on the amount adsorbed

(b) $K_c V \ll 1$; $$\delta = K_c n \delta_c. \qquad (6)$$

The complexes are "weak." Most of the active centers are not occupied. The line shifts in the NMR spectra are independent of the amount of the substance adsorbed.

In the intermediate case the inverse dependence of the line shifts on the adsorption values should be nonlinear [Eq. (4)].

Let us now return to the experimental data.

A linear inverse dependence of the line

shifts in NMR spectra on the adsorption, for unsaturated molecules, provides evidence for the formation of "stable" surface complexes. Such a dependence was observed earlier for benzene adsorbed on Aerosil with cobalt ions (*12*). For saturated hydrocarbons adsorbed on the cobalt samples the inverse dependence of the shifts on the adsorption values is nonlinear. This provides evidence for the formation of rather weak complexes. As the line shifts are very small in the spectra of paraffins adsorbed on the Aerosil surface with bivalent nickel ions, either no complexes are formed or they are very unstable.

Let us attempt to estimate the stability of surface complexes. The simplest case is hydrogen adsorption. Indeed according to Eq. (6) at sufficiently high temperatures the shift for weak complexes would not depend on the amount of the substance adsorbed, but would exponentially increase with a decrease of temperature:

$$\delta = K_c \cdot n\delta_c = K_c^0 e^{\Delta H/RT} n\delta_c. \qquad (7)$$

This is just the case for hydrogen adsorption on zeolites containing CO^{2+} and Ni^{2+} ions at temperatures below 270°K (Fig. 6). The slopes of the straight lines correspond to ΔH values of about 4 kcal/mol. The heat of complex formation is equal to the sum of this value and the heat of physical adsorption of hydrogen.

To calculate the strength of hexane complexes with Co^{2+} ions we used experimental data on the temperature dependence of the shifts at various adsorption values. The Arrhenius plot of the equilibrium constants calculated from Eq. (4) is shown in Fig. 7. The heat of complexation is about 2 – 2.5 kcal/mol larger than the value of the heat of physical adsorption. Unfortunately it is impossible to calculate the heats of complexation for unsaturated hydrocarbons. However, they are obviously higher than corresponding values

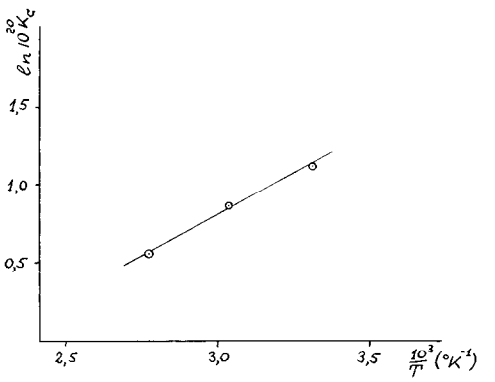

FIG. 7. The Arrhenius plot of the equilibrium constant for complex formation of *n*-hexane with Co^{2+} ions.

for saturated hydrocarbons and molecular hydrogen.

Now let us discuss the nature of the surface complexes. As shown above by the spectral measurements, the CO^{2+} and Ni^{2+} ions on Aerosil surface are tetrahedrally or trigonally coordinated. Although on the basis of optical spectra one cannot choose between these two types of coordination, we shall consider the structure of active centers in terms of trigonal coordination, because in tetrahedral coordination the ions are screened by the ligands situated along the z axis. On the contrary the trigonal coordination which is close to D_{3h} symmetry is suitable for complexation.

For discussion of the structure of the surface complexes let us use the wave functions of tetrahedral transition metal ions which are shown in Fig. 8 (*14*). For trigonally coordinated Co^{2+} ions the d_{z^2} orbital is half filled, whereas that of the Ni^{2+} ions is occupied by an electron pair. The remaining unpaired electrons of these ions are in $\phi_2 \sim d_{x^2-y^2}$ and $\phi_3 \sim d_{xy}$ orbitals.

Such a structure of surface active centers is supported by experimental results obtained by a study of complexes with benzene molecules. With Co^{2+} ions the bonding in these complexes may arise due to overlapping of the d_{z^2} orbital with the lowest filled π-orbital of the benzene molecule. Interaction of filled orbitals of

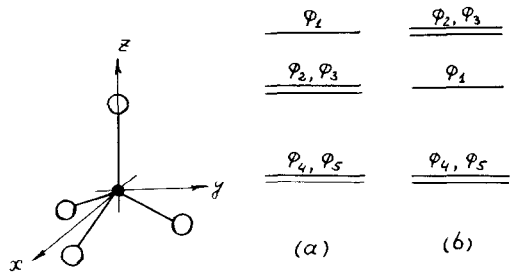

FIG. 8. Energy level splittings and wave functions of a single $3d$ electron in trigonally distorted tetrahedral coordination. $\phi_1 = d_{z^2}$; $\phi_2 = \alpha d_{x^2-y^2} - \beta d_{xz}$; $\phi_3 = \alpha d_{xy} + \beta d_{yz}$; $\phi_4 = \beta d_{x^2-y^2} + \alpha d_{xz}$; $\phi_5 = \beta d_{xy} - \alpha d_{yz}$. (a) z-axially compressed tetrahedron; (b) z-axially elongated tetrahedron and trigonal coordination.

the ions with antibonding orbitals of ligands can also contribute to coordination bonding. However, in the first order of perturbation theory it would not affect the distribution of spin density in the system. Much smaller shifts in the case of bivalent nickel are explained by the different symmetry of benzene π-orbitals and half filled $d_{x^2-y^2}$ and d_{xy} orbitals of these ions (*15*). Thus the formation of surface complexes involving benzene molecules would depend on the electronic structure of the adsorption centers. As shown below this is also true for complexes involving saturated hydrocarbons.

The nature of the bonding of unsaturated molecules (C_2H_4, C_3H_6, C_6H_{10}) with bivalent cobalt and nickel ions seems to be similar to that of benzene complexes. Both d_{z^2} and ϕ_2 and ϕ_3 orbitals can contribute to the formation of the complexes with Co^{2+} ions. For Ni^{2+} ions in which the d_{z^2} orbital is occupied by an electron pair, only ϕ_2 and ϕ_3 orbitals can contribute to complex formation (Fig. 9). Regardless of the ion orbitals involved in the formation of surface complexes, there arises positive spin density in the π-systems of the coordinated molecules of unsaturated hydrocarbons. This causes the shift of the lines of the protons at the double bonds to higher fields (*16*). The lines of the propylene methyl group and cyclohexene protons show shifts to lower fields.

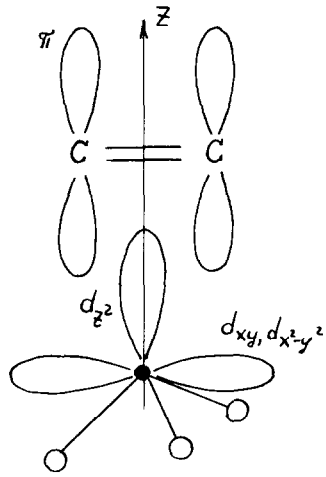

FIG. 9. The bonding in surface π-complexes of olefins with Co^{2+} or Ni^{2+} ions.

When considering the structure of the complexes of saturated hydrocarbons with surface CO^{2+} ions, one should take into account that their NMR spectra do not show any difference in the paramagnetic shifts of the lines caused by various protons. This can be explained by assumption of the complex structure given in Fig. 10. In this case, interaction of a Co^{2+} d_{z^2} orbital with a localized molecular orbital of a CH bond would prevail in coordination binding. Such coordination would result in

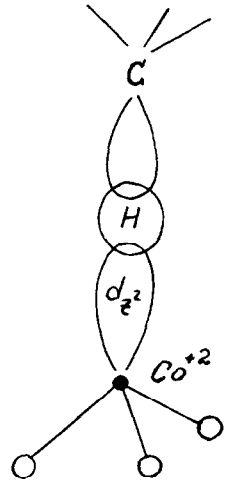

FIG. 10. The bonding in surface complexes of saturated hydrocarbons with a Co^{2+} ion.

negative spin density at the coordinated H atom and a positive one at the carbon atom adjacent to it. The extension of spin density on other atoms of the ligands would be negligible as in σ-electron radicals. Since the energy characteristics of various CH bonds of saturated hydrocarbons are similar, one could expect a fast exchange between various coordinated structures and as a result the NMR spectra would consist of a single line with the same shifts for all protons of coordinated molecules.

A similar coordination structure was postulated earlier for complexes of halomethanes (such as CH_3Cl, CH_2Cl_2, etc.) with nitrogen-containing stable radicals (*17–19*). For these complexes a proton resonance shift to high fields was observed in agreement with our results reported here.

When interpreting the NMR spectra we suggested that the line shifts observed are mainly caused by contact interaction of unpaired electrons of the ions with protons of coordinated molecules. This assumption is supported by the fact that in tetrahedral complexes of bivalent cobalt and nickel the pseudocontact interaction as a rule is small (*20–21*). Further evidence is the opposite direction of the line shifts observed in the NMR spectra of molecules of similar geometry adsorbed on Co^{2+}-containing Aerosil (*12*).

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