Paramagnetic shifts were measured, by the method of dilution with a large excess of ligand, for Co(II) and Ni(II) acetylacetonate complexes with pyridine N-oxide and its α- and β-methyl derivatives in which it is assumed that the complex has a $\text{M(AA)}_2 \cdot 2\text{N-oxide}$ composition. It was shown that the paramagnetic shifts in the Ni(AA)$_2 \cdot 2\text{N-oxide}$ complexes are dependent on the contact interaction, and there is a considerable contribution by the pseudocontact interaction in the Co(AA)$_2 \cdot 2\text{N-oxide}$ complexes; in both cases, the unpaired electron is found in the $\pi$-system of the ligand. From an analysis of the pseudocontact interaction in the Co(AA)$_2 \cdot 2\text{N-oxide}$ complexes, it was found that the N-O-M angle equals 129°. It was also shown that large paramagnetic shifts for the protons of the CH$_3$-group of the acetylacetonate-ion in the Co(AA)$_2 \cdot 2\text{N-oxide}$ complexes are dependent on the basic pseudocontact interaction.

In recent years, the high resolution NMR method has found interesting applications in the investigation of still another class of compounds—the complex compounds of paramagnetic ions [1, 2]. Unusually large "paramagnetic" shifts in the NMR spectra of such compounds are dependent on two types of interactions: contact and pseudocontact [3]. Contact shifts yield a distribution pattern of the spin density according to the ligand, and the pseudocontact shifts in some cases make it possible to obtain information on the geometrical structure of the complex.

Indexing of the contact and pseudocontact shifts were first presented by Hope and Ward [4] for Co(II) and Ni(II) acetylacetonate complexes with pyridine, and by Horrocks, Taylor, et al. for similar complexes with isonitrile and triphenylphosphine [5].

In this work, the paramagnetic shifts for the Co(II) and Ni(II) acetylacetonate complexes with pyridine N-oxide (PyO) and α- and β-methylpyridine-N-oxide (α-MePyO and β-MePyO respectively) were measured. The indexing of these shifts for their contact and pseudocontact components are presented. On the basis of the data obtained, conclusions on the delocalization mechanism of the spin density in the ligands and on the geometric structure of the complex are made.

**EXPERIMENTAL**

A weighed portion of the cobalt or nickel acetylacetonate (≈0.02 g) was placed into an ampoule, equipped with a stopper, used for taking NMR spectra, and dissolved in chloroform. Weighed portions of the N-oxide were successively added to the solution we obtained. After each addition, the NMR spectra were taken. The NMR spectra were taken on a JNM-3 instrument at a frequency of 40 Mcps at room temperature. Tetramethylsilane ($\delta = 0.00$), hexamethyldisiloxane ($\delta = 0.06$), and cyclohexane ($\delta = 1.43$) served as the internal standard. Cobalt and nickel acetylacetonate were prepared according to the method described in [6]; all the N-oxides were dried over phosphorus pentoxide.

**THE NMR SPECTRA AND THE CONCENTRATION DEPENDENCE OF THE LINE POSITIONS**

The shape of the NMR spectra and line references in some of the systems we studied are shown in Fig. 1. In Figs. 2 and 3, the relation of the chemical shifts of the N-oxide protons to the ratio of the M(AA)$_2$ acetylacetonate

---

*We used the term "paramagnetic" for designating the components of the shift dependent on the interaction of the nucleus with the unpaired electrons in the complex. The sign of the shift can be either positive or negative.*
Fig. 1. The shape of the NMR spectra of the Co(II) and Ni(II) acetylacetonate N-oxide complexes: a) PyO + Co(AA)$_2$; b) α-MePyO + Co(AA)$_2$; c) α-MePyO + Ni(AA)$_2$.

Fig. 2. The relation of the shifts to the ratio of the Ni(AA)$_2$ concentration to the α-MePyO concentration.

concentration to the overall concentration of the N-oxide are shown. The linear plot of the curves for large excesses of N-oxide indicates that complexes of only one type are present in the system, whose ligands rapidly interchange with the free ligand. The fact that the constancy of the signal of the shift for the CH$_3$-groups in the Co(II) acetylacetonate-ion complexes fits the linear portions of the curves (Fig. 3) is further confirmation of this. Since the ligand is present in a large excess, it is of course assumed that the complex has a M(AA)$_2$·2N-oxide composition.

The values of the paramagnetic shifts for all the systems we studied are presented in the table. The experimental paramagnetic shifts were determined from the slopes of the linear portions of the curves (the method for the theoretical calculation of the shifts in the Co(AA)$_2$ complexes is presented below).

**DISCUSSION**

1. Ni(AA)$_2$ Complexes with N-oxides. Distribution of the Spin Density

As is known, the paramagnetic shifts in the pyridine Ni(AA)$_2$ complexes [4], and the benzonitrile and triphenylphosphine Ni(AA)$_2$ complexes [5] are dependent exclusively on the contact interaction. The series of data, which