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Complex Nickel (Ii) Compounds Based on Acylhydrazones of Aroyltrifluoracetylmethhanes

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A B S T R A C T
The article is devoted to the synthesis of nickel(II) complex compounds based on acylhydrazones of aroyltrifluoromethanes and their IR-PMR spectra.

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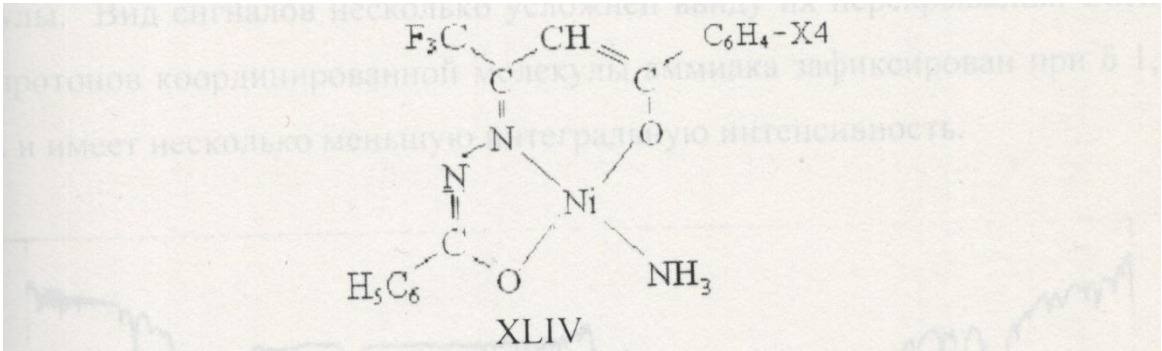
By reacting ammonia solutions of nickel(II) acetate and alcohol solutions of H_2L^1-H_2L^5 in an equimolar ratio, complex compounds NiL^1 *NH_3 -NiL^5*NH_3 were obtained. Based on the results of elemental analysis, IR and PMR spectroscopy data, the complexes were assigned the structure



XLIV

X = H ($NiL^1 \cdot NH_3$); CH_3 ($NiL^2 \cdot NH_3$); OCH_3($NiL^3 \cdot NH_3$); Cl ($NiL^4 \cdot NH_3$); Br ($NiL^5 \cdot NH_3$).

The IR spectra of complex compounds differ from the IR spectra of free ligands in that there are no absorption bands in the region of 1660-1700 and 3400 cm-1. This indicates deprotonation of the ligands during complex formation. In many ways, the IR spectra of the obtained complex compounds XLIV are identical to the IR spectra of the studied complex compounds NiL^1 * NH_3 (XLIV); stretching vibrations at 1595-1706 cm-1 are characteristic. (VC=N) and a single band at 1520-1530 cm-1.(V N=C-O). For example, in the IR spectrum of the complex compound NiL^5 *NH_3, the band of relatively weak intensity at 1073 cm-1 (Fig. 8) belongs to (V N -N), which is shifted to the high frequency region by 8-10 cm-1 compared to the spectrum of free ligand (1,4,7,)

The isolated nickel(II) complex compounds turned out to be diamagnetic in solutions of various solvents; the results of studying the NMR spectra and diamagnetism allow us to conclude that the obtained nickel(II) complex compounds have a planar-square structure (XLIV structure).

As an example, consider the PMR spectrum of a complex compound

NiL_3 *NH_3 (Fig. 9, a). In the NMR spectrum of the NiL_3 *NH_3 complex in a DMSO-d_6 solution, a signal of a single vinyl proton is observed at δ 4.68 ppm.

Multiplet signals centered at δ 7.37, 7.71 and 8.05 ppm. are caused by protons of the aromatic nuclei of the hydrazone and β-diketone fragments of the molecule. The appearance of the signals is somewhat complicated due to their overlap. The signal from the protons of the coordinated ammonia molecule was detected at δ 1.38 ppm. and has a slightly lower integral intensity.

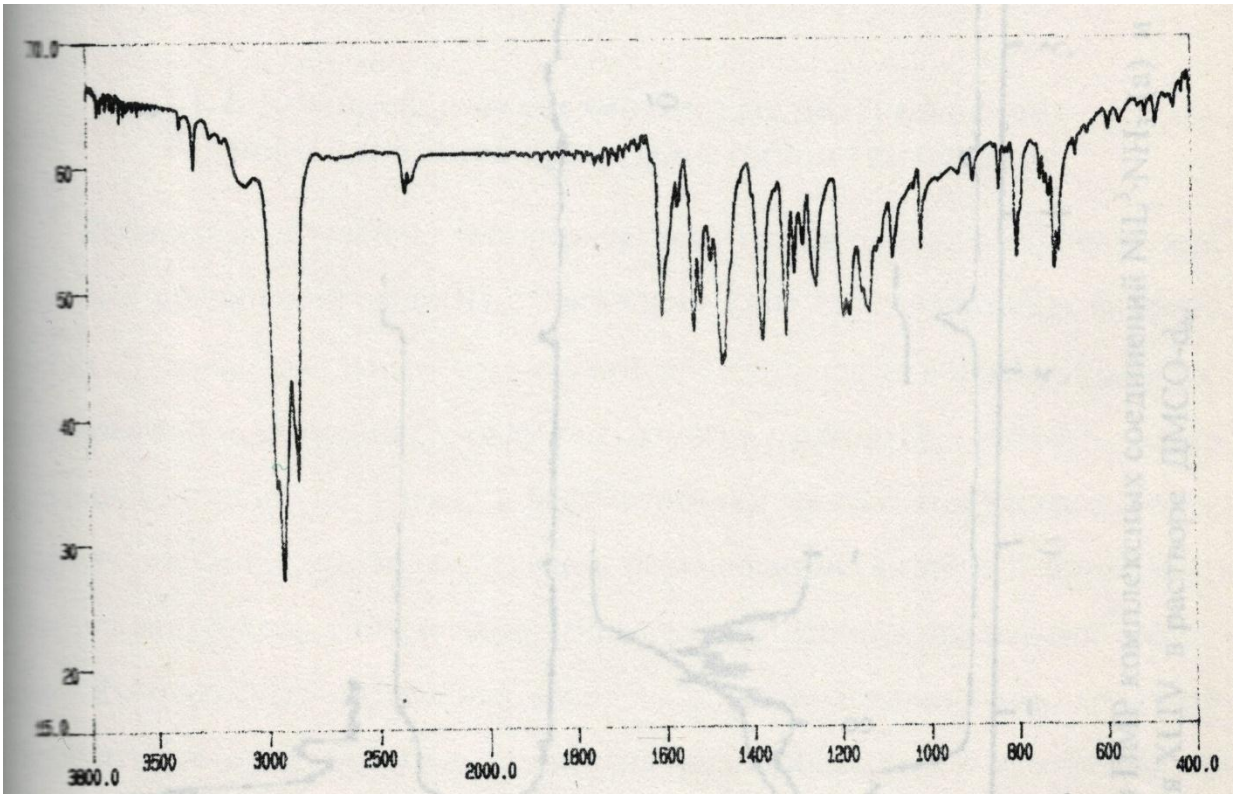


Рис. 8. ИК спектр комплексного соединения никеля(II) $NiL^5 \cdot NH_3$ строения XLIV на основе 1-бензоил-3-(4-бромфенил)-5-гидрокси-5-трифторметил-2-пиразолина (H_2L^5).

This, in our opinion, is explained by the partial replacement of the ammonia molecule with a donor solvent molecule. PMR spectrum of a complex compound

NiL_5 *NH_3 is somewhat different from the spectrum of NiL_3 *NH_3 in that in it the signals of the terminal protons are partially shifted to the low-field region. The signal from the proton of the vinyl part of the molecule resonates at δ 4.76 ppm. Signals from protons of aromatic substituents have a more complex form and appear at δ 7.44; 7.58; 7.75; 7.81; 8.19 ppm A weak signal from the protons of the coordinated ammonia molecule was detected at δ 1.36 ppm (Fig. 9b). The somewhat high-field shift of the signal from the vinyl proton should be explained by the formation of d-π type dative bonds between the d-electrons of nickel(II) and the π-orbital of the conjugated system of five- and six-membered metallocycles [8,9,10].NiL^5 *NH_3

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