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COMPLEXES OF AZOLES WITH ACETYLACETONATES

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A number of the most important inorganic biological systems are coordination adducts formed as a result of the axial addition of azoles to chelates of the transition metals [1].

We have synthesized adducts by heating solutions of azoles (L), acetylacetone (A), and metal (nickel, cobalt, and vanadyl) chlorides in methanol or an aqueous methanol mixture with the addition of NH_4OH up to pH ~ 7-8. According to the results of elementary analysis, the adducts of the nickel and cobalt acetylacetonates have the $MA_2 \cdot 2L$ composition, as compared with the $MA_2 \cdot L$ composition in the case of vanadyl chloride, regardless of the basicity of the azoles and steric factors. The following imidazoles were used: imidazole, N-ethylbenzimidazole, benzimidazole, 3,5-dimethylpyrazole, and benzotriazole (the pK values range from 7.02 to 1.60).

A systematic increase in most of the frequencies of the deformation vibrations of the coordinated donors as compared with the free azoles is observed in the IR spectra of mineral oil suspensions of the adducts, and this constitutes evidence [2] for localization of the coordinate bond on a nitrogen atom of the pyridine type. The frequencies increase regularly in the order $Co < Ni < VO$, and this is associated with an increase in the stability of the adducts in the same order. The decreases in the $\nu_{C=O}$ bands of the acetylacetonates (~20 cm^{-1}) upon adduct formation are independent of the nature of the metal and the azole ring. The basicity and the volume of the heterocyclic fragment have little effect on the decrease in the frequency of the vibrations of the vanadyl group ($\Delta\nu = 50\text{-}70\ cm^{-1}$) during complexing.

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