

Synthesis, structure and properties of coordination compounds of copper(II) and cobalt(II) with nitrogen containing heterocyclic cations

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Abstract

Novel coordination compounds of copper(II) and cobalt(II) with 3-amino-2-chloro-5-methylpyridine (**3-L**¹) and 2-(chloromethyl)pyridine (**2-L**²) such as (**3-L**¹H)₂[CuCl₄]·H₂O (**I**), (**3-L**¹H)₂[CuCl₄]·2H₂O (**II**), (**3-L**¹H)₂[CoCl₄] (**III**), (2-L²H)₂[CuCl₄] (**IV**), (2-L²H)₂[CoCl₄] (**V**), (2-L²H)₂[CuBr₄] (**VI**), have been synthesized. Compounds have been investigated by means of X-Ray diffraction analysis, TGA, DSC. It is shown that the cation structure is influenced by the mutual arrangement of the substituent in the pyridine ring. In the 5-amino-2-chloro-3-methylpyridine (**5-L**¹) compound, the chlorine atom deactivates the pyridine ring, this leads to an increase in the concentration of unprotonated pyridine. In the isomeric molecule of 3-amino-2-chloro-5-methylpyridine (**3-L**¹), the deactivating effect of chlorine is eliminated due to the positive mesomeric effect of the amino group. Under acidic conditions, in the case of competing processes of protonation of the organic base and its complexation with 3d-metal ions of the first transition series, the equilibrium shifts toward the protonation reactions in the amino group of the **5-L**¹ molecule and the nitrogen atom of the pyridine ring of the **3-L**¹ compound. For copper(II) compounds with **3-L**¹, the effects of thermo- and solvatochromism are observed, in which a reversible color transition is green ↔ yellow. It is shown that in chlorocuprate(II) complexes, the molecules of crystallization water are structure-forming due to the formation of hydrogen bonds and determine the geometry of the coordination polyhedron [CuCl₄]²⁻. In **I**, **IV**, **VI** compounds an anion [CuHal₄]²⁻ has the structure of a distorted tetrahedron, and in **II** complex there is a flat-square structure. The tetrahedral structure of **III** and **V** complexes is typical for cobalt(II) tetrahalides. Structural features and hydrogen contacts are well indicated by spectral analysis methods (IR and electronic (DRS) spectroscopy). The relationship between the wavelength of reflected light and the angle Hal-M-Hal of the coordination polyhedron is found. It is shown that a decrease in the deviation of the Hal-M-Hal angle from the ideal in the halide complexes of copper(II) and cobalt(II) leads to an increase in the value of the wavelength.

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