

First coordination polymer based on diterpenoids. Synthesis, structure, and magnetic properties*

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One-dimensional coordination polymer was obtained by cation exchange reaction of triethylammonium salt of methyl *ent*-16 α -*H*-phosphonyloxybeyeran-19-oate with CuCl₂. Its structure was determined by single crystal X-ray diffraction analysis. The formation of hydrophilic channels consisting of phosphorus containing fragments, copper atoms, and water, which are framed by hydrophobic surroundings from tetracyclic bulky beyeran substituents, is observed in the crystal. The study of the temperature dependence of the static magnetic susceptibility of the polymer indicates a weak antiferromagnetic interaction between the copper spins.

Key words: diterpenoids, isosteviol, beyerane, hydrophosphoryl compounds, coordination polymer, magnetic susceptibility.

The diterpenoid isosteviol is a promising chiral platform widely used in the last years in asymmetric organic synthesis.¹ It is easily available from renewable natural raw materials by acid hydrolysis of the glycoside stevioside present in the plant *Stevia rebaudiana* Bertoni. This compound has such attractive properties as enantiomeric purity; a large enough content (up to 10%) in the natural material and its easy isolation; the presence of active groups available for functionalization; configurational stability of chiral centers and high stereoselectivity in modification. A series of preceding works (ours and of other authors) was devoted to the chemical modification of isosteviol,² its use in supramolecular chemistry for development of molecular receptors,³ synthesis of tweezer-structures and macrocycles,⁴ phosphorylation processes.⁵ However, isosteviol and its derivatives have not been yet used in the chemistry of metal complex compounds. At the same time, its derivatives which contain the groups capable of coordination transition metals could have served as ligands for development of chiral magnetoactive complexes. Sometimes, chirality of the ligand gives additional properties related to the spin asymmetry on such materials. The preparation of such chiral magnetic system is of interest not only from the point of view of fundamental studies of magnetochiral

effects, but also as a possibility of their use for the development of new magneto-optical devices. Apart from that, such compounds are expected to exhibit new effects allowing one to control magnetic properties of solid materials.⁶ Therefore, the synthesis and studies of molecular structure of chiral complexes of magnetoactive metals is an actual problem.

The purpose of the present work is the synthesis and studies of the structure and magnetic properties of the first coordination polymer based on Cu^{II} containing isosteviol beyerane frameworks as chiral organic substituents.

Results and Discussion

It is well known that organophosphorus compounds are excellent complexation agents in the reaction with transition metal salts, which lead to the formation of stable complexes with a complicated three-dimensional architecture. Among the phosphorus-containing complexation agents, nonchiral molecules are encountered the most frequently. Phosphorus compounds with chiral substituents are used in the complexation reactions much less often.⁷ Even rarer the phosphorus atom bears substituents with the fragments of complicated natural molecules containing asymmetric centers.⁸ Recently, we have obtained new hydrophosphoryl compounds with chiral fragments of isosteviol.⁵ In particular, the reaction of methyl *ent*-16 α -

* Dedicated to Academician of the Russian Academy of Sciences R. Z. Sagdeev on the occasion of his 75th birthday.