Zeolitic imidazolate frameworks (ZIFs) are an outstanding class of MOFs, constructed from tetrahedrally configured transition metal cations linked through bridging imidazolate (Im) spacers. ZIFs are structurally isomorphic to zeolites since the metal-Im-metal angle is similar to the Si–O–Si angle (145°) in the latter compounds. This feature was exploited to produce a huge variety of porous transition metal-based ZIFs. Our initial goal was to combine Im and alkaline metal borohydrides in the same structure with the formation of porous borohydride compounds, where Im serves as a structural unit of the framework, while borohydride anions provide with a functionality. However, alkali and alkaline earth metal-based imidazolates are not structurally characterized so far. Thus, the coordination chemistry of Im towards alkali and alkaline earth metal cations remains a challenge. With this in mind and inspired by the storage properties of ZIFs, we have recently turned our attention to Im-based coordination compounds with Li⁺, Na⁺ and K⁺ [1]. Unfortunately, these imidazolates form dense and hypercoordinated structures. The coordinative demand of the metal cation increases with an increase of the ionic radii. The Li⁺ cation exhibits a strong propensity to form heteroleptic structures, while the K⁺ cation allows to coordinate the Im ring through the π-system.

Our next challenge was to obtain magnesium imidazolate (MgIm₃), which, based on the nature of Mg²⁺ as well as its coordination chemistry, was considered as a much more promising complexing agent in comparison with alkaline metal cations. While, the freshly synthesized MgIm₃ was found to be amorphous, annealing at relatively high temperatures yields the crystalline and porous MgIm₃.

Herein, we present our results on the synthesis, characterization and some properties of newly obtained MgIm₃.


Keywords: zeolitic imidazolate framework, magnesium imidazolate, porous structure, crystal structure, physical properties

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Polydentate molecules are of growing interest as they are widely applied as scaffolds in the combinatorial synthesis of artificial receptors for ions with medical and environmental potential. Among the broad variety of synthetic molecules, polyazaoxa ligands have received special attention due to their outstanding coordination abilities. A particular goal involves the construction of ligands with an appropriate order and predictable arrangement of two or more molecular components with possibility to form hydrogen bonds, which play the pivotal role in molecular recognition by synthetic receptors.

Herein, we present a study on the crystal structures of a series of novel polydentate N,O-ligands possessing unsymmetrical urea fragments attached to a p-cresol scaffold. The compounds are obtained by a fast and simple protocol from p-cresol-based symmetrical bis-amine, phosgene, and primary amine. Their structures are assigned by 1D and 2D NMR spectra in solution and by single crystal XRD in solid phase. Ortep drawings of selected crystal phases are presented on Figure 1.

The ligands can be generally divided in two groups: open-chain substituted aromatics with at least one unsymmetrical urea unit (a) and fused aryloxazinones with unsymmetrical urea fragment (b). The concept is to design polydentate ligands with variable coordination abilities controlled by the difference in the molecule geometry.

The single crystal XRD analysis showed that the open-chain substituted molecules are oriented towards optimal intramolecular H-bonding of the ureas’ heteroatoms, while the preferred geometry of oxazinones is driven by intermolecular bonding.

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